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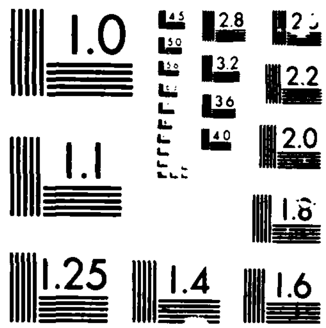
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AD-A176 013

TECHNICAL MEMORANDUM 86/222
November 1986

OPTIMIZATION OF THE FINNIGAN MAT 5100 CAPILLARY GAS CHROMATOGRAPH-MASS SPECTROMETER FOR THE ANALYSIS OF POLYCHLORINATED BIPHENYLS

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ABSTRACT

The basis of operation of a capillary gas chromatograph with a quadrupole mass spectrometer as a detector is reviewed. This is followed by the description of the optimization of a Finnigan MAT 5100 gas chromatograph-mass spectrometer-data system (GC/MS/DS) for the detection and identification of PCBs. In particular, the effects of increasing electron multiplier voltage and the use of multiple ion detection (MID) scan sequences on the sensitivity of the quadrupole mass spectrometer are investigated. Both increasing the electron multiplier voltage and the use of specialized MID scan sequences were found to result in an improved detector response.

RÉSUMÉ

On examine le principe d'un chromatographe en phase gazeuse à colonne capillaire couplé avec un spectromètre de masse quadripolaire, qui sert de détecteur. On décrit ensuite l'optimalisation d'un chromatographe en phase gazeuse Finnigan MAT 5100 avec spectromètre de masse et système de traitement des données (CG/SM/TD), qui servira à la détection et à l'identification des PCB. On a étudié, en particulier, les effets de l'augmentation de la ténsion appliquée au multiplicateur d'électrons et de l'utilisation de séquences de balayage pour la détection d'ions multiples (DIM) sur la sensibilité du spectromètre de masse quadripolaire. On a ainsi constaté que le fait d'augmenter la tension appliquée au multiplicateur d'électrons et d'utiliser des séquences de balayage spécialisées pour la DIM permettait d'améliorer la réponse du détecteur.

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NOTATION PAGE

A_{XY}	multiple ion detection descriptor that is a part of the scan sequence A1
A1	multiple ion detection scan sequence
amu	atomic mass unit
B	baseline subtract
Cl^{35}	chlorine atom with nominal mass 35
Cl^{37}	chlorine atom with nominal mass 37
dc	direct current
dm	mass interval
DS	data system
e	charge on an electron, 1.602×10^{-19} Coulombs
EC	electron capture
EI	electron impact
EPA	Environmental Protection Agency
EX	extractor (voltage)
EZ	electrometer zeroing routine
eV	electron volt
$FeCl_3$	ferric chloride
GC	gas chromatograph
GC/MS	gas chromatograph-mass spectrometer
IE	ion energy
IP	ion programming
L	lens (voltage)
m	mass

m/e	mass to charge ratio
M	minimum peak area
MID	multiple ion detection
M^+	molecular or parent ion
PCB(s)	polychlorinated biphenyl(s)
ppm	parts per million
Q1	multiple ion detection scan descriptor
RIC	reconstructed ion chromatogram
RH	resolution high (mass)
RL	resolution low (mass)
rf	radio frequency
r_0	radius of cylinder defined by quadrupole rods
T	threshold
t	time
τ	period ($\omega t/2$)
V	volt
V_{ac}	radio frequency voltage
V_{dc}	direct current voltage
W	minimum peak width
ω	frequency of the rf voltage in radians/second

1.0 INTRODUCTION

The use of polychlorinated biphenyls (PCBs) as dielectric fluids in electrical transformers and capacitors has been commomplace over the last fifty years. PCBs, first commercially produced in the 1920s, are excellent dielectric fluids as a result of their thermal stability, low flammability, favorable dielectric constant and resistance to oxidation and hydrolysis. They are generally produced by the chlorination of biphenyl using anhydrous chlorine and ferric chloride ($FeCl_3$). The number and percentage of each of the polychlorinated biphenyls produced depends upon the time the reaction is allowed to proceed. Table 1 lists the ten chlorinated biphenyls, from the mono to the deca chloro compounds, and the number of structural isomers possible for each of these chlorinated biphenyls.

The chemical inertness of polychlorinated biphenyls led to their accumulation in the environment. In 1966, the detection of PCBs that had accumulated in envir[illegible]ntal samples led to a renewed interest in the analysis and toxicit[illegible]se compounds(1). As concerns over the adverse effects of PCB[illegible]ilife and humans increased, their commercial production slo[illegible] was finally banned in the USA in 1977 (2). Nonetheless, it is estimated that over 80 percent of the PCBs manufactured for electrical applications in transformers and capacitors remained in service. In Canada, the total PCBs still in service were estimated at 17,000,000 kg in 1982 (3).

In closed systems such as transformers and capacitors, PCBs are disposed of when the equipment containing them is taken out of service or when the dielectric fluid is replaced during routine maintainance. PCBs are then destroyed through incineration or are stored in a secure chemical landfill. The proper disposal of PCB contaminated wastes is described in Reference 3.

Often it is not obvious if a transformer or capacitor fluid contains or is contaminated with PCBs. At present, a PCB contaminated material is defined as a liquid or solid containing in excess of 50 parts per million (ppm) PCBs (3,4). Solutions containing less than 50 ppm PCBs have been treated in a legal sense as if they contained no PCBs (4). This has been challenged in the courts in the USA. The EPA criteria was deemed arbitrary and the final allowable limit will undoubtably be less than 50 ppm. More recently, it has been suggested that the identification and quantitation of PCBs should be directed towards determining the levels of certain of the more toxic individual PCB isomers (5,6). Therefore, the ability to identify and quantitate PCBs in general and individual isomers in particular at levels below 50 ppm will be necessary and desirable.

The concern for the safe handling and disposal of PCBs and PCB contaminated materials has necessitated the development of analytical

techniques that allow the detection of PCBs, often at trace levels. PCBs have been detected using packed column gas chromatography (GC) with electron capture (EC) detection (7-10), capillary column GC with EC detection (8-11), and GC (either packed or capillary column) coupled with a quadrupole mass spectrometer as a detector (5,9,12).

The use of a mass spectrometer (MS) as a detector for a gas chromatograph has several advantages over the standard gas chromatographic detectors (such as the electron capture detector, flame ionization detector, or thermal conductivity detector). For instance, standard gas chromatographic detectors cannot positively identify the chemical compounds giving rise to the peaks in a chromatogram when a single column is used. Samples received for PCB analysis are often dissolved in matrices such as hydrocarbon based oils that may contain compounds with retention times and response factors similar to those of polychlorinated biphenyls. Matrix interferences can suggest the presence of PCBs when they are not present. To ensure that PCBs are present requires the use of a second column with a different packing. Further, standards similar to the sample being studied are needed to provide a basis on which to identify the chromatographic peaks, i.e., injections of the sample and standard are made on two different columns to ensure that the sample and standard match is not fortuitous on any one column. Gas chromatography-mass spectrometry (GC/MS) not only gives the basic chromatographic information on a mixture of compounds, i.e., retention time, size, shape, and number of peaks, but also allows positive identification of the compounds in the mixture by way of their mass spectra. In qualitative analysis no standards are required to confirm the presence of a compound as the mass spectra of the compounds eluting from the column provide the basis for identification because mass spectra are specific for individual compounds.

Commercially available PCB mixtures contain a number of PCB isomers. The ability to positively identify the polychlorinated biphenyls giving rise to the peaks in the chromatogram greatly facilitates the unambiguous interpretation of results for aged or weathered samples, where the more volatile and water soluble isomers may be reduced in concentration with respect to the other isomers. Such identification was difficult with GC/EC detection as standard PCB mixtures were often used to generate fingerprint data; that is, retention times, shape and number of peaks, for these compounds. If the peaks corresponding to the lighter PCBs are diminished in intensity or are not seen at all due to weathering of the sample, then matching of fingerprints for sample and standard becomes more difficult and the identification less certain. The use of fingerprint information becomes much less important with MS detection as each peak can be used to generate the mass spectra of the compound that gave rise to it. The mass spectral fragmentation pattern of a compound is characteristic of that species and allows its positive identification.

This paper describes the operation of a Finnigan MAT 5100 gas

chromatograph-mass spectrometer-data system (GC/MS/DS) and its optimization for the detection and identification of polychlorinated biphenyls (PCBs). The effect of increasing the electron multiplier voltage and using several scanning procedures, i.e., full and multiple ion detection (MID) scans, on the sensitivity of the mass spectrometer as a PCB detector is investigated and discussed.

2.0 INSTRUMENTATION - THE CAPILLARY GC/MS

2.1 Capillary GC

A capillary gas chromatograph is shown diagrammatically in Figure 1. It consists of an injection port where the sample to be analysed is introduced, a column where the components of the sample are separated, and the plumbing to allow a carrier gas to transport the sample components through the column.

The components of the mixture are separated on the column as a result of their partitioning between the stationary phase on the column and the carrier gas. The preference of individual compounds for the stationary phase or the carrier gas is governed by distribution coefficients which are characteristic of a particular compound and vary from one compound to another. Thus a mixture of compounds is separated as it moves through the column and its constituents arrive at the detector at different times.

Separations on capillary columns are characterized by good resolution and narrow peak profiles. The resolution is due to the the length of the column, generally between 15 and 60 m in length, which results in a large number of theoretical plates.

2.2 Mass Spectrometer

The three major components of the Finnigan MAT 5100 quadrupole mass spectrometer, i.e., the electron impact (EI) ionization source, the quadrupole mass analyser, and the electron multiplier, are described in the following sections.

2.2.1 The Electron Impact Ionization Source

As a compound elutes from the capillary column of a GC/MS system, it enters the ionization source. For this work, an electron impact (EI) ionization source was used. An EI ionization source consists of a filament and reflector, collector, ion volume, extractor, and lens, and is shown diagrammatically in Figure 2. A brief description of the EI source follows.

The filament provides a source of electrons which impact the molecules eluting into the ion volume. These electrons, which are produced by the thermionic emission of an electrically heated filament which is kept at a negative potential (generally -70 eV) relative to the walls of the ion source, have an energy approximately equal to the negative potential on the filament.

The collector, located opposite the filament, is kept at a constant +30 V to attract electrons from the filament through the ion volume. As the electrons move through the ion volume they impact the molecules that have eluted from the column causing the molecules to lose electrons and form positive ions. The masses and number of the ions produced is a function of the bond strengths of the molecule being impacted. The walls of the ion source are positively charged so that the positive ions produced form a cloud in the middle of the ion volume. The potential applied to the ion volume is termed the ion energy (IE). As it is important that all ions enter the quadrupole filter with the same velocity, the ion energy is programmed to increase as the mass range is scanned from low to high masses. The programmed increase in the ion energy is referred to as ion programming (IP).

The side of the ion volume closest to the quadrupole mass filter is the extractor (EX) and it is kept at a positive potential lower than that of the ion volume to create a voltage gradient. The gradient between the extractor and the ion volume causes the positive ions to move towards the extractor. The lens (L), which lies behind the extractor and outside the ion volume, is negatively charged and focuses the ion beam for optimum entrance into the quadrupole mass filter.

2.2.2 Quadrupole Mass Filter

The Finnigan MAT 5100 GC/MS utilizes a quadrupole mass filter as its detector. The formal theory of the quadrupole mass filter is based on field forming surfaces which are hyperbolic cylinders. A brief description of the formal theory of this detector follows.

In a hyperbolic field the motion of ions in the x and y directions are described by the Mathieu equations (11), which are as follows:

$$d^2x / d^2\tau + (a + 2q \cos 2\tau)\ x = 0$$

$$d^2y / d^2\tau - (a + 2q \cos 2\tau)\ y = 0$$

where $a = 8eV_{dc}/mr_o{}^2\omega^2$, $q = 4eV_{ac}/mr_o{}^2\omega^2$, $\tau = \omega t/2$, V_{dc} is the dc voltage, V_{ac} is the rf voltage, e is the charge of an electron, r_o is the radius of the cylinder defined by the quadrupole rods, and ω is the frequency of the rf voltage. These equations are characterised by regions of stability and instability, i.e., the amplitude of x or y remains

bounded in the former case and increases without limit in the latter. Whether the trajectory of an ion is stable or not depends solely on the values of a and q. For an ion to pass through the quadrupole mass filter and arrive at the electron multiplier, its trajectory must be stable for both x and y components of velocity. In addition, its amplitude of oscillation must be less than r_o. It has been found that round cylinders, in place of hyperbolic cylinders, provide a suitable compromise to the difficulty in constructing hyperbolic cylinders. Round cylinders are used in the the quadrupole MS at DREA.

A combination of radio frequency (rf) and direct current (dc) voltages is applied to each diagonally paired set of rods and both the rf and dc voltages are ramped functions which vary with time. The rf voltages applied to each pair of rods are 180 degrees out of phase. For a given ratio of the dc and rf voltages, a line can be drawn through the origin of a q versus a plot (see Figure 3). Each point on this line corresponds to a particular value of the mass-to-charge ratio (m/e) of the ions being produced in the source. The interval, dm, of this value which lies within the stable part of the q versus a plot corresponds to the ions of masses with stable trajectories. If the ratio of dc to rf voltages is increased, the slope of the scan increases and passes closer to the apex of the stability diagram. The interval (dm/m) then decreases and the resolving power of the spectrometer (m/dm) increases.

At any given time, t, a particular set of rf and dc voltages are being applied to the quadrupole rods. Under this particular set of conditions only ions of a certain m/e value can oscillate through the rods and reach the detector. All other ions with m/e values different from this particular mass to charge ratio undergo unbounded oscillations and strike the quadrupole rods.

The quadrupole mass filter operates in a scanning mode. By ramping the rf and dc voltages all ions in a specified mass range (m/e) are tuned through the detector in a scan. The resulting detector trace, called a reconstructed ion chromatogram (RIC), is a plot of the total ion current arriving at the electrometer during each scan against the retention time of the compound or compounds eluting from the column that gave rise to those ions.

The sensitivity of the mass spectrometer for a particular compound is directly related to the amount of time that the detector is tuned to observe the ions that are characteristic of the mass spectral fragmentation of that compound. If the quadrupole mass spectrometer scans from 40 to 400 atomic mass units (amu) in 2 seconds, then each mass is tuned through the rods for 2/360 seconds. This procedure is somewhat inefficient. For example, if the mass spectrum of the compound of interest is well known, then masses of the ions of greatest intensity for that compound can be determined. Then instead of scanning the mass range from 40 to 400 amu, the quadrupole mass analyzer can be programmed to look

for ions in a narrower range or ions of a particular mass. Such scans are termed multiple ion detection (MID) scans and are used to increase the sensitivity of the mass spectrometer as a detector. The ions reaching the electrometer during a MID scan are those that are characteristic of the compound of interest and proportionately more time during each scan is available for the detection of the compound of interest.

2.2.3 Electron Multiplier

The electron multiplier in the Finnigan MAT 5100 GC/MS consists of three components: a conversion dynode, a voltage dropping resistor, and a continuous dynode electron multiplier. It is shown diagrammatically in Figure 4. The voltage on the electron multiplier assembly, which can be controlled by the operator of the GC/MS, is applied to the conversion dynode and to the electron multiplier by way of a voltage dropping resistor. The negative potential on the conversion dynode attracts positive ions which have been tuned through the quadrupole mass spectrometer. When these positive ions strike the dynode surface, electrons are released by impact ionization and are forced by the field gradient into the cathode of the electron multiplier.

The cathode of the electron multiplier acts to amplify the current produced by the electrons coming from the conversion dynode. The gain of the electron multiplier can also be controlled by the operator of the GC/MS. It is generally set at 10^7, although it can be set at 10^6 or 10^8.

By varying the voltage on the conversion dynode, the kinetic energy of the ions striking the conversion dynode is varied. Increasing the kinetic energy of the ions striking the dynode increases the number of electrons released by the dynode. Consequently the response of the detector is increased. For a given concentration of compound entering the ion volume the response of the GC/MS as a detector can be maximized by finding the optimum electron multiplier voltage.

2.2.4 Sources of Noise

The noise found in chemical instrumentation is characterized by spikes in the acquired data and is generally short in duration and low in intensity. It can be the result of power supply problems, vibration, aging of the electrical components including the electron multiplier and preamplifier, and X-ray radiation that passes the shield to the electron multiplier. Noise can be removed or minimized in two ways: by hardware zeroing and/or software zeroing.

On the Finnigan MAT 5100 GC/MS/DS the hardware zero can be set either manually or automatically. The hardware zero acts to eliminate noise from the mechanical and electronic parts of the system by setting the response baseline above the mean noise in the system. It is reset whenever the electrometer range is changed.

The software zero acts in conjunction with the hardware zero. It defines the criteria used by the computer (data system) to determine whether a response should be seen as a peak and recorded or as noise and eliminated. These criteria, which are operator defined, are:

-the threshold below which all data is eliminated,
-the baseline subtract value that eliminates data below that value,
-the minimum width of a response that is seen as a peak, and
-the minimum peak area that is read as a peak.

The threshold does not eliminate peaks that exceed it in value, i.e., if a peak exceeds the threshold value then the entire peak is retained. By proper selection of these variables, spurious responses that are most often the result of noise can be minimized.

3.0 EXPERIMENTAL

3.1 Equipment

All GC/MS analyses were carried out on a Finnigan MAT 5100 gas chromatograph/mass spectrometer with a SuperIncos data system. A Finnigan model 9611 capillary gas chromatograph with a Durabond-1 (30 meter long x 0.25 millimeter inside diameter) capillary column (100% methyl silicone) was used for all separations. The GC oven was temperature programmed as follows: 80°C for two minutes, then ramped to 150°C at a rate of 20°C/minute and finally ramped to 300°C at a rate of 4°C/minute. The temperature program is shown graphically in Figure 5.

The mass spectrometer was run in the electron impact (EI) mode using an ionizing voltage of 70 electron volts (eV). Typical values of the ion energy (IE), ion program (IP), lens voltage (L), extractor voltage (EX), and resolution settings (RL and RH) are shown in Table 2 along with the range of values that these parameters can assume. Hardware zero was set automatically with the program EZ, while the software zeroes, i.e., threshold (T), baseline subtract (B), minimum peak width (W), and minimum area (M), were set to the values shown in Table 2.

The spectrometer was generally tuned so that sensitivity was favored over resolution, i.e., the ratios of the intensities of the 219, 414, and 502 peaks of the calibration gas (perfluorotributylamine) were respectively at least 30%, 1.4% and 0.8% of the intensity of the 69 peak.

3.2 Standards

Commercial PCB mixtures: Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, and Aroclor 1260, were obtained from PolyScience Corporation, Niles, Illinois, USA, as 100 ppm solutions in hexane. One microliter injections of the PCBs were introduced into the column in the modified splitless mode. Capillary gas chromatographs can be operated in the split or splitless mode. In the split mode the injector is swept by

a split gas which carries away some of the sample and reduces the amount of sample introduced onto the column. However, in the splitless mode the splitter is turned off. This results in a much greater amount of the sample being introduced to the column for analysis. In the modified splitless mode, the split valve was turned off until 45 seconds after the injection which allows a greater percentage of the sample to be swept into the column by the carrier gas.

The Aroclor mixtures, produced by Monsanto, are identified by a four digit code. For example, the 1232 designation of Aroclor 1232 refers to two things: the first two digits indicate biphenyl and the last two digits indicate the average weight percent of chlorine in the PCB mixture. The average molecular compositions (weight percent) of the five Aroclor mixtures used in this work are listed in Table 3a, while Table 3b lists some characteristics of these Aroclor mixtures.

3.3 Scan Sequences

GC/MS data were acquired for the five standard PCB solutions using three scan sequences.

The first utilized a scan from 50 to 500 atomic mass units (amu) in 2 seconds. The average percentage of mono, di, tri, tetra, penta, hexa, hepta, octa, and nonachlorobiphenyls in Aroclors 1232, 1242, 1248, 1254, and 1260 are shown in Table 3a. By displaying the mass spectrum of the peaks of the reconstructed ion chromatogram (RIC) for each of the Aroclors, it was possible to determine the major ions of the electron ionization mass spectra and to measure a range of retention times for the various PCB groups, i.e., the mono, di, tri, ... and nonachlorobiphenyls. Once the major ions and retention times of the individual PCBs were known, multiple ion detection (MID) sequences could be written which greatly enhanced the sensitivity of the mass spectrometer as a detector.

The second scan sequence, designated Q1, was comprised of a single MID scan. Instead of scanning over a range of m/e values, the mass selective analyser was set to tune through ions of m/e values characteristic of PCBs. Q1 scanned for the most abundant ions of the various PCBs, i.e., the mono, di, tri,...and nonachlorobiphenyls which were taken from the mass spectra acquired using the full scan mode from 50 to 500 amus. MID Q1 is shown in Figure 6. The blocked areas represent the masses that are tuned through the quadrupole mass filter during each scan.

The third scan sequence, designated A1, is comprised of several MID scans similar to Q1. One of the MID scans is shown in Figure 7 while the others are listed in Appendix A. The MID scan that is operative varies as the GC run procedes. Sequence A1 acts to change the masses that are tuned through the quadrupole by activating the MID scans sequentially as the retention times of the isomers in a PCB mixture increase, i.e., sequence A1 is composed of MID scans which tune through ion fragments particular to

the PCBs eluting from the capillary column at a given time during the GC run.

4.0 RESULTS AND DISCUSSION

Reconstructed ion chromatograms (RIC) of five standard Aroclors, i.e., Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, and Aroclor 1260, are shown in Figures 8a through 8e respectively. The chromatograms are the result of 1 microlitre injections of 100 ppm solutions of the Aroclors in hexane acquired using a full scan from 50 to 500 amu. It can be seen that the retention time envelope, i.e., the times of elution of the first and last PCBs in a mixture, of the polychlorinated biphenyls in the various Aroclors moves to longer retention times as the weight percent of chlorine in the PCB mixture is increased, i.e., from 32 to 42 to 48 to 54 to 60% for Aroclors 1232, 1242, 1248, 1254, and 1260 respectively.

Two MID sequences are described in the following section and the resulting increase in sensitivity for the detection of PCBs discussed.

4.1 Multiple Ion Detection

As indicated in the Introduction, the sensitivity of the mass spectrometer as a detector for a particular compound or compounds is directly related to the amount of time during a scan sequence that ions characteristic of the compound or compounds are tuned through the detector. In the full scan mode, for instance over the mass range from 50 to 500 amu, a large percentage of the scan time is spent looking for ions that are not characteristic of the species of interest.

Mass spectra of typical PCBs, from the mono to the deca chlorinated compounds, acquired on the Finnigan MAT 5100 GC/MS are shown in Appendix B. The molecular ion (M^+) or parent ion, i.e., the ion formed when the compound loses an electron, is the ion of greatest intensity (base ion) for the majority of PCBs. The most noticeable effect in the mass spectra of PCBs is due to the isotopic abundance of chlorine, i.e., monochlorobiphenyl is characterised by M^+ and $(M+2)^+$ peaks in a ratio of 3:1 as a result of the natural abundance of the Cl^{35} and Cl^{37} atoms. Similarly, dichlorobiphenyl, which contains two chlorine atoms, displays peaks at M+2 and M+4 in addition to M^+, trichlorobiphenyl peaks at M+2, M+4, and M+6 in addition to M^+ and so on. The relative intensity of these peaks can be determined from the natural abundances of the Cl^{35} and Cl^{37} atoms.

As the mass fragmentation patterns of the polychlorinated biphenyls are known, selection of single ions or ions in smaller mass ranges that are characteristic of the electron impact fragmentation of PCBs allows a greater percentage of the fragment ions to be detected. Both approaches, i.e., more selective mass ranges and multiple ion detection, have been trialed and the results are discussed below.

The MID descriptor Q1 is shown diagrammatically in Figure 6. Descriptor Q1 instructs the quadrupole mass spectrometer to scan for ion fragments with m/e values between 148 and 152, 182 and 192, 218 and 228, 253 and 262, 289 and 297, 323 and 336, 357 and 370, 381 and 396, 425 and 442, and 460 and 478 amus. These mass ranges are typical of the molecular or parent ions of the mono, di, tri, ... octa and nonachlorobiphenyls respectively.

The RICs for Aroclors 1232, 1242, 1248, 1254, and 1260 acquired using MID Q1 are shown in Figures 9a through 9e respectively. A 1 microlitre injection of a 100 ppm solution of each of the Aroclors was used to obtain these RICs. Comparison of the RICs for Aroclor 1232, acquired using a full scan from 50 to 500 amu and that from the MID sequence Q1 are shown in Figures 8a and 9a respectively. The mass spectrometer detected the same PCBs coming off the capillary column when either the full scan or MID Q1 was used, but the response for the individual PCBs of Aroclor 1232 was enhanced with MID Q1 as compared to that with the full scan from 50 to 500 amu, i.e., the count numbers in the upper right hand corner of the Figures are much larger when Q1 is used (44416 versus 5808 for the most intense peak), indicating that more ions are being detected.

Although the scan descriptor Q1 increases the amount of time during each scan that is spent on detecting ions characteristic of PCBs (as compared to a full scan from 50 to 500 amu), it does not take full advantage of the multiple ion detection capabilities of the GC/MS/DS. For instance, if a dichlorobiphenyl is eluted from the column, ionized, the fragment ions tuned through the quadrupole mass spectrometer and detected, the time the analyser spends looking for ion fragments greater than the molecular weight of a dichlorobiphenyl is wasted.

A MID descriptor, written to consider retention time ranges of the various PCBs, could eliminate scanning mass ranges or masses that are not characteristic of the PCBs eluting from the column at that particular time.

Development of this MID descriptor sequence involved determining the retention times of the various PCB isomers on the capillary column. This information allowed time windows to be defined where groups of PCB isomers were most likely to elute. As there was some overlap of retention times, i.e., some dichlorobiphenyls were found to elute after some of the trichlorobiphenyls, the individual MID descriptors that constituted the MID descriptor sequence had to include m/e values for the PCBs that might elute during a particular time range.

Such a MID descriptor sequence has been developed. It changes the m/e values of the ions that are tuned through the detector as a function of the retention times of the various PCB isomers. The MID descriptor sequence is listed in Table 4 and the individual MIDs shown

diagrammatically in Figure 7 and Appendix A. The individual MIDs that constitute the final sequence are identified by subscripts that refer to the number of chlorine atoms in the PCBs being detected, i.e., A13 scans for m/e values characteristic of mono, di, and trichlorobiphenyls and A45 for tetra and pentachlorobiphenyls.

The RICs for Aroclors 1232, 1242, 1248, 1254, and 1260 acquired using MID descriptor sequence A1 are shown in Figures 10a to 10e respectively. Again, it can be seen that the RICs are similar to those produced using a scan from 50 to 500 amus or the MID descriptor Q1. However, the response has increased over that found with Q1 for example. The RICS for Aroclors 1242 and 1260, acquired with the three scan modes, are compared in Figures 11a and 11b respectively. The scale of the y-axis has been normalized to that found using MID descriptor sequence A1 so that the variation in detector response for a 100 ppm solution of an Aroclor, as the scan mode is changed from the full scan mode to MID descriptor Q1 to MID descriptor sequence A1, can be seen. The responses of the various isomers in these two Aroclors increase significantly as the quadrupole mass analyser is instructed to tune through ions with m/e values that are characteristic of the PCBs eluting from the capillary column.

4.2 Effect of Varying Electron Multiplier Voltage

Figures 12a to 12d show the RICs of one microlitre injections of 100 ppm solutions of Aroclor 1254 in hexane where the electron multiplier voltage has been varied from 1300 to 1900 volts in 200 volt increments. The chromatograms were acquired in the full scan mode (50 to 500 amus in 2 seconds) and the responses normalized to that for the scan with the electron multiplier voltage set at 1900 volts. It can be seen that the response of the detector increases monotonically as the electron multiplier voltage is increased from 1300 to 1900 volts.

However, as the voltages on the conversion dynode and the cathode of the electron multiplier are increased further, a point is reached where the detector is saturated. Analysis of saturated data can lead to rapid deterioration of the electron multiplier assembly and subsequent failure. The final magnitude of the voltage applied to the electron multiplier is dictated by the amount (concentration) of the material to be analysed. If maximum sensitivity is required, the voltage on the electron multiplier can be increased to the point where the data becomes saturated. If more concentrated samples are available the voltage can be turned down to a lower level. The critical factor is that increased sensitivity results in accelerated deterioration of the electron multiplier assembly.

5.0 SUMMARY

The optimization of the Finnigan MAT 5100 GC/MS/DS for the detection of PCBs has been described. It has been shown that the sensitivity of the

mass spectrometer as a detector for PCBs can be greatly enhanced through the use of multiple ion detection and multiple ion detection sequences over that achieved through the use of full scan modes. Further, the sensitivity of the detector can be increased by selection of an optimum electronmultiplier voltage when working with samples containing trace amounts of analyte.

Table 1

The number of isomers possible for each of the ten chlorinatedbiphenyls($C_{12}H_{10-n}Cl_n$). The molecular weight of each of the ten chlorinatedbiphenyls is also listed.

n	name	# of isomers	M.W. *
1	monochlorobiphenyl	3	188.7
2	dichlorobiphenyl	12	223.1
3	trichlorobiphenyl	24	257.6
4	tetrachlorobiphenyl	42	292.0
5	pentachlorobiphenyl	46	326.4
6	hexachlorobiphenyl	42	360.9
7	heptachlorobiphenyl	24	395.3
8	octachlorobiphenyl	12	429.8
9	nonachlorobiphenyl	3	464.2
10	decachlorobiphenyl	1	498.7

* M.W. - molecular weight

Table 2

Typical values of the instrument parameters (electron impact source and software zeroes) used for the Finnigan MAT 5100 GC/MS.

electron impact ionizing voltage (EI)		-70.0 eV
ion programming voltage (IP)		9.4 V
extractor voltage (EX)		7.0 V
resolution setting	- low (RL)	129
	- high (RH)	136
electron multiplier voltage (ES)		1600 V
threshold (T)		8
baseline subtract (B)		0
minimum peak width (W)		5
minimum peak area (M)		3

Table 3a

The average make-up (weight percent) of the five Aroclors used in this study (n refers to the number of chlorines on the biphenyl molecule).

Aroclor

n	1232	1242	1248	1254	1260
0	6				
1	26	1			
2	29	13	1		
3	24	45	21	1	
4	15	31	49	15	
5		10	27	53	12
6			2	26	42
7				4	38
8					7
9					1

Table 3b

Some characteristics of Aroclor mixtures.

	Aroclor				
	1232	1242	1248	1254	1260
density (g/cm^3 @ 20^oC)	1.26	1.38	1.44	1.54	1.62
viscosity (Saybolt 100^oC)	31-32	34-35	36-37	44-58	72-78
distillation range (^oC)	270-325	325-366	340-375	365-390	385-420
vaporization rate ($g/cm^2/h$) x 10^6	874	338	152	53	13
solubility in H_2O (25^oC) mg/L x 10^2	-	24	5.2	1.2	0.3

Table 4

The times that the various MID descriptors that comprise the sequence AI are engaged during a GC/MS run.

Window #	MID descriptor	Scan cycles	Time on	Time off
1	*	60	0.00[a]	2:00
2	A12	290	2.00	11:40
3	A23	90	11.40	14:40
4	A34	120	14.40	18:40
5	A45	70	18:40	21:00
6	A56	80	21:00	23:40
7	A67	150	23:40	28:40
8	A78	340	28:40	40:00

* - filament and electron multiplier turned off for the first two minutes of the run.

a - times listed as minutes and seconds

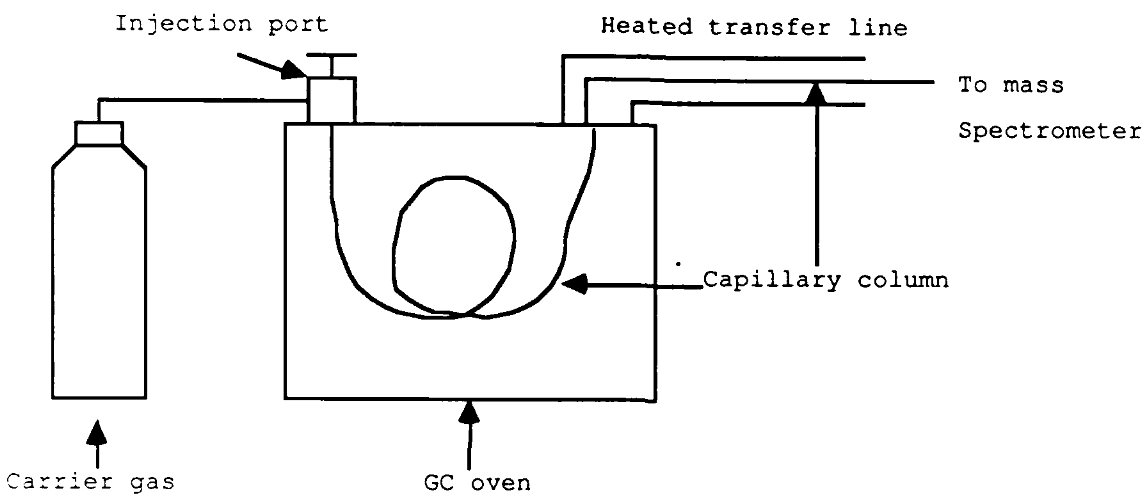


Figure 1 - Diagrammatic representation of a capillary gas chromatograph.

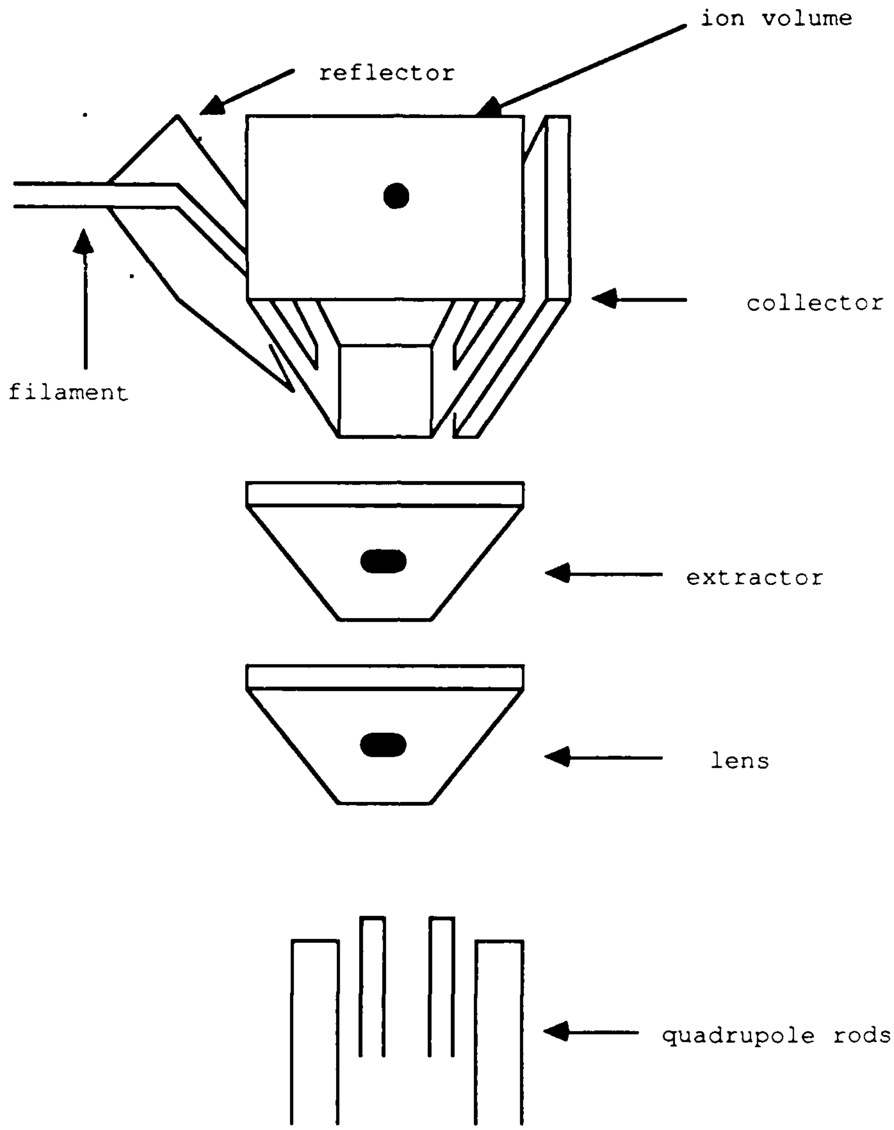


Figure 2: Diagrammatic representation (exploded view) of the electron impact (EI) source of a Finnigan MAT 5100 GC/MS.

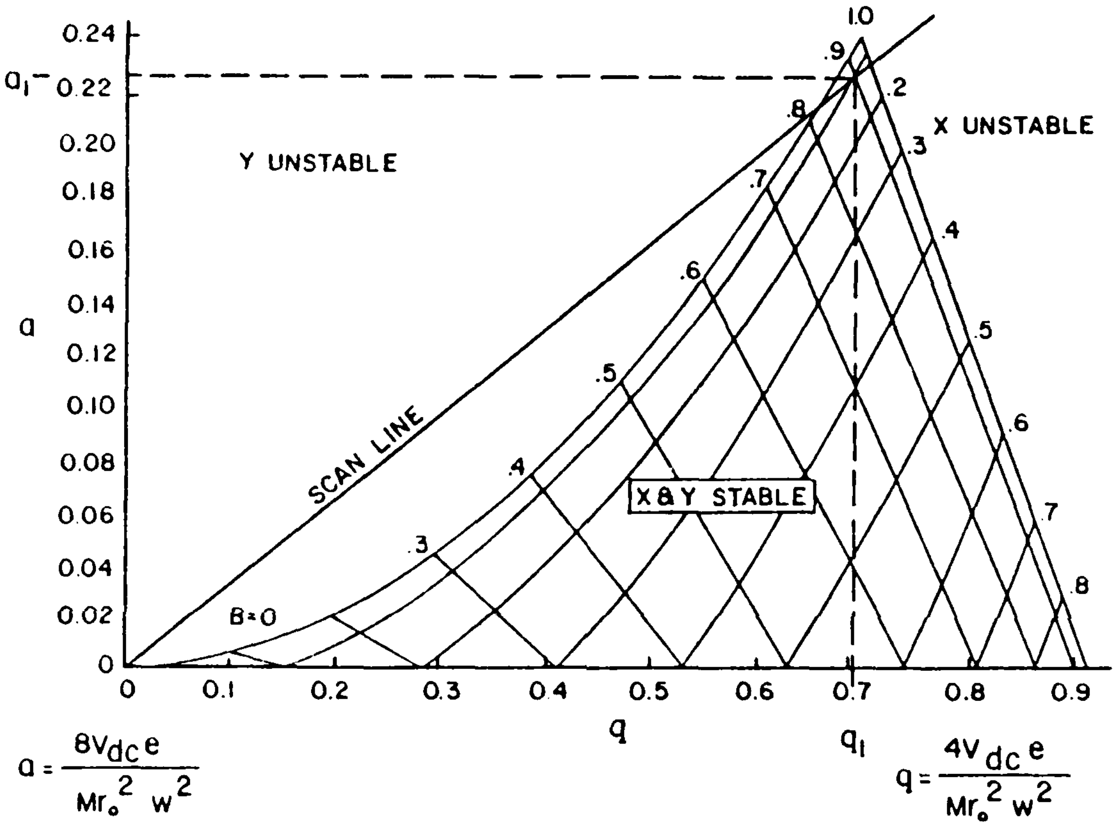


Figure 3 - A q versus a plot showing the stable and unstable regions of the x and y components of the ions trajectory through the quadrupole mass filter. The interval of the scan line that lies within the stable portion of the q versus a diagram corresponds to masses with stable trajectories.

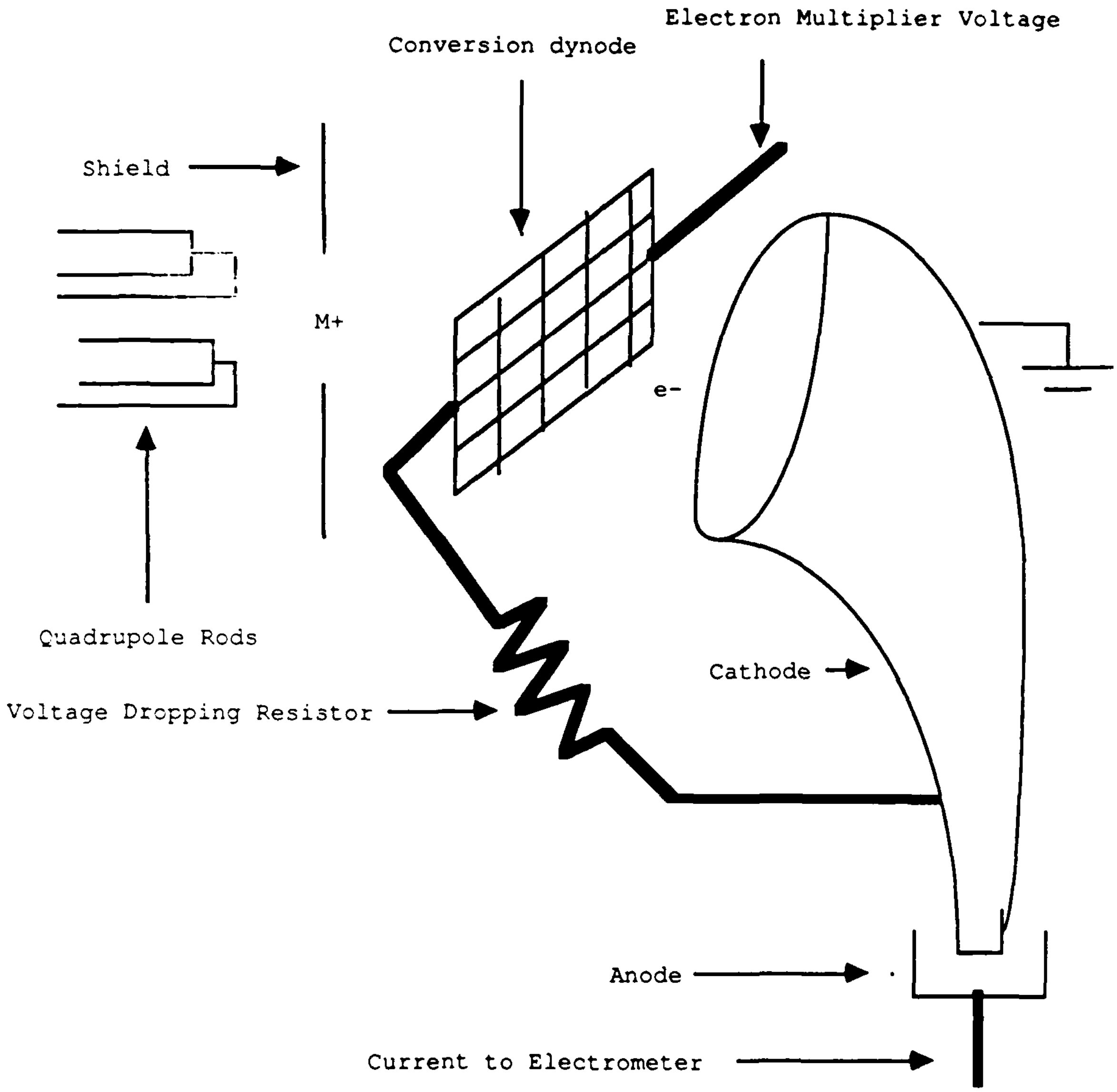
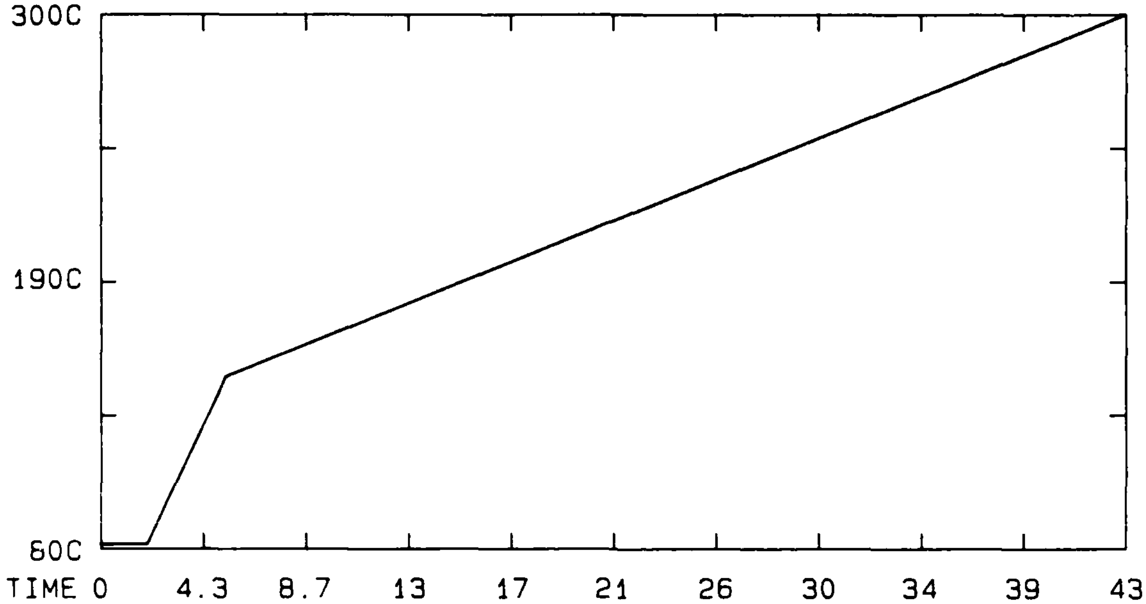
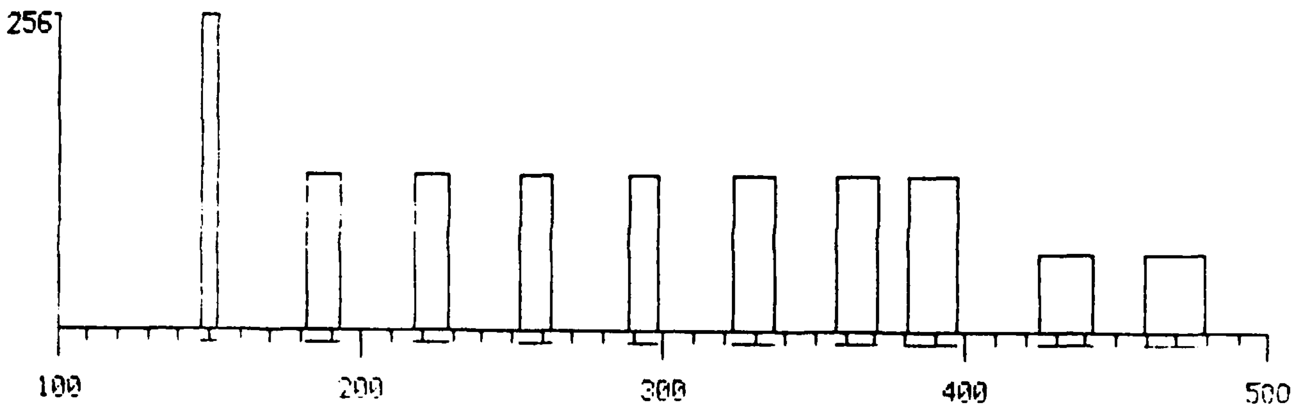


Figure 4: Diagram of the electron multiplier used in the Finnigan MAT 5100 GC/MS.



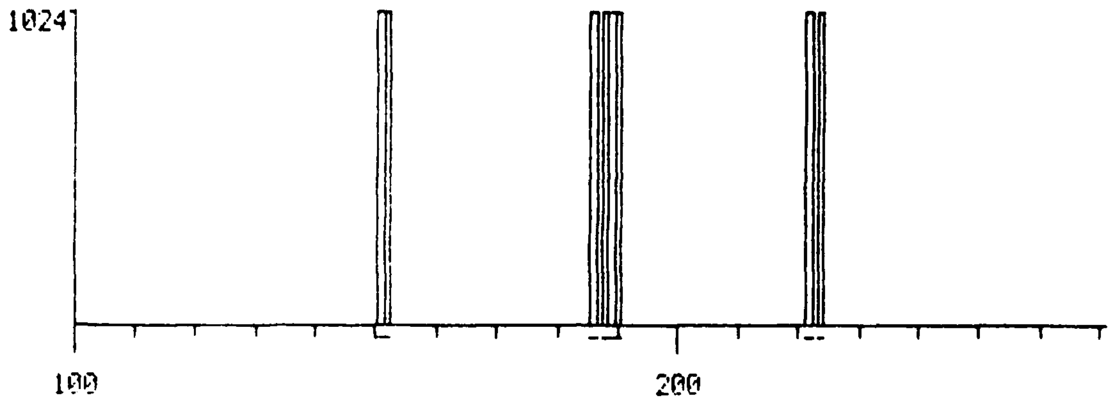
FROM TEMP (C)		TO TEMP (C)	RATE (C/M)	TIME (MIN)	TOTAL TIME (MIN)
80	-	80	-	2.0	2.0
80	-	150	20.0	3.5	5.5
150	-	300	4.0	37.5	43.0

Figure 5 - Temperature program used to control the oven of the Finnigan 9611 gas chromatograph during PCB analysis.



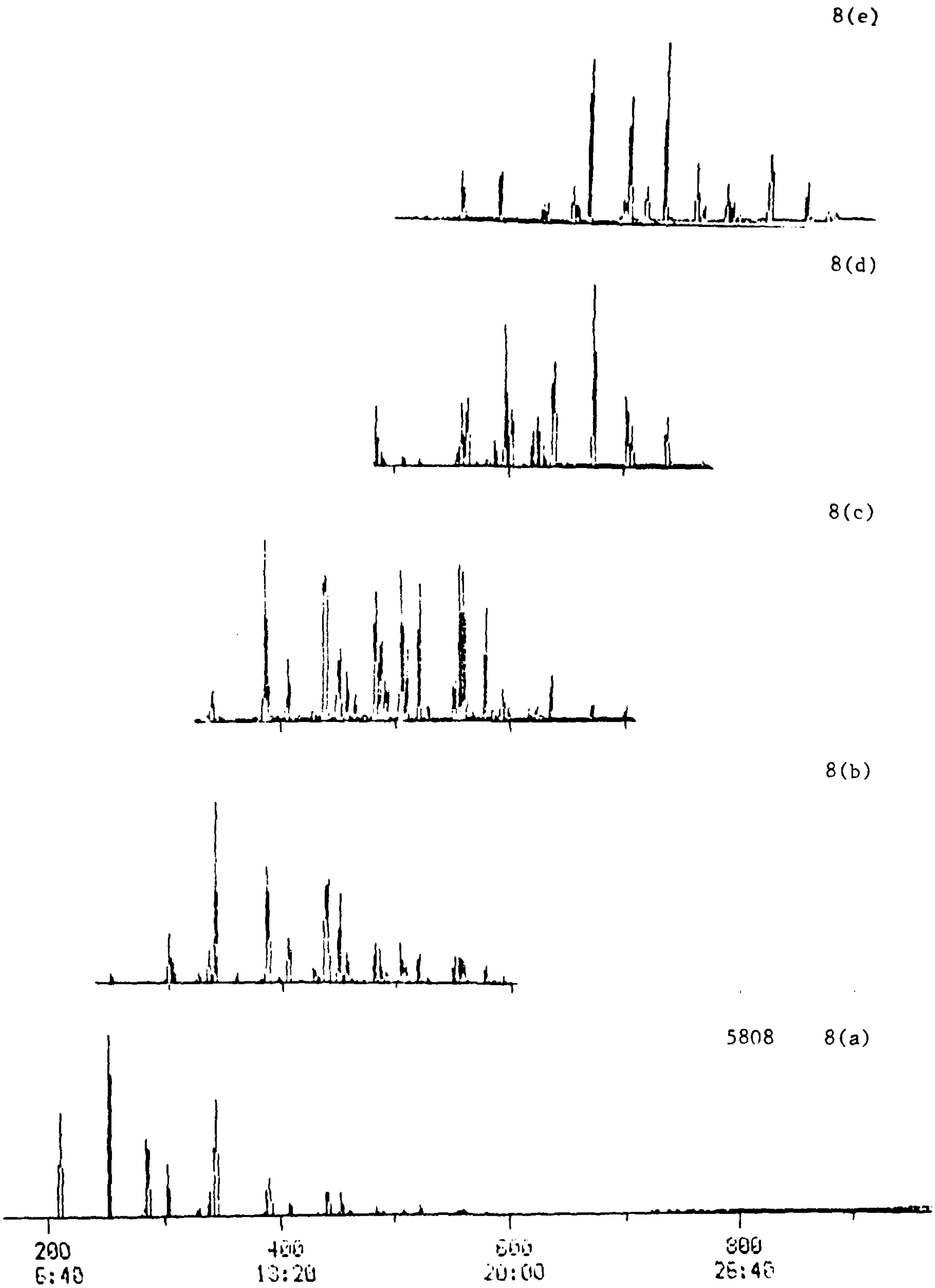
INT #	BEGIN MASS	END MASS	TIME REQUEST	(SECS) ACTUAL	MPW	MFW	MA	TH	BL	ION
1.	147.500	152.500	0.200	0.165	3	80	5	1	0	POS
2.	181.500	192.500	0.200	0.182	3	80	5	1	0	POS
3.	217.500	228.500	0.200	0.182	3	80	5	1	0	POS
4.	252.500	262.500	0.200	0.165	3	80	5	1	0	POS
5.	288.500	297.500	0.200	0.149	3	80	5	1	0	POS
6.	322.500	336.500	0.200	0.231	3	80	5	1	0	POS
7.	356.607	370.611	0.200	0.232	3	80	5	1	0	POS
8.	380.614	396.618	0.200	0.265	3	80	5	1	0	POS
9.	424.627	442.632	0.200	0.149	3	80	5	1	0	POS
10.	459.638	478.643	0.200	0.157	3	80	5	1	0	POS

Figure 6 - Diagram of the MID descriptor Q1. The blocked areas indicate the masses that are tuned through the quadrupole during each scan. The masses or mass ranges scanned are listed below the schematic.

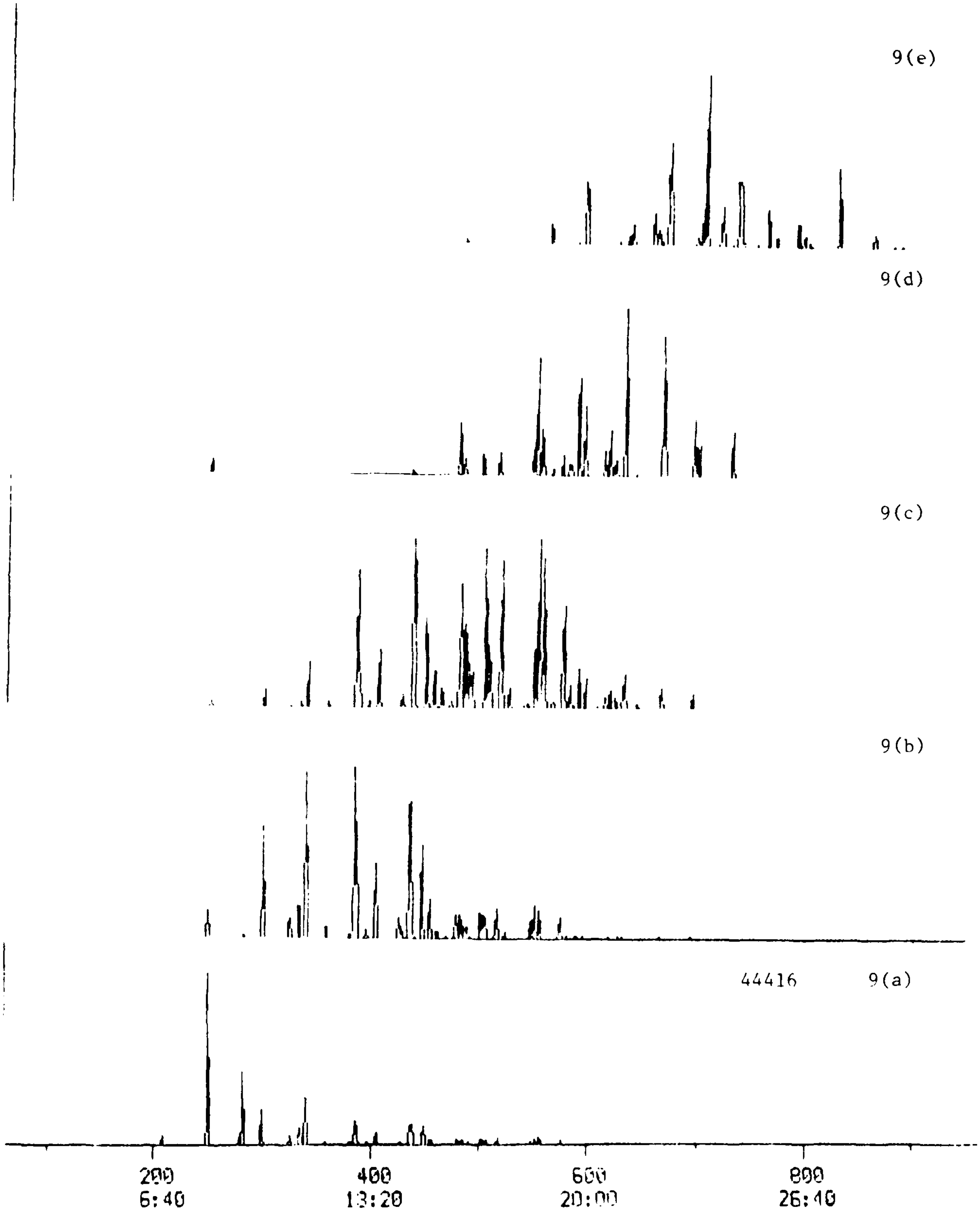


INT #	BEGIN MASS	END MASS	TIME REQUEST	(SECS) ACTUAL	MPW	MFW	MA	TH	BL	ION
1.	150.394	151.394	0.150	0.133	3	80	10	1	0	POS
2.	151.394	152.394	0.150	0.133	3	80	10	1	0	POS
3.	185.370	186.370	0.150	0.133	3	80	10	1	0	POS
4.	187.368	188.368	0.150	0.131	3	80	10	1	0	POS
5.	188.368	189.368	0.150	0.133	3	80	10	1	0	POS
6.	189.368	190.367	0.150	0.133	3	80	10	1	0	POS
7.	221.345	222.345	0.150	0.133	3	80	10	1	0	POS
8.	223.343	224.343	0.150	0.133	3	80	10	1	0	POS

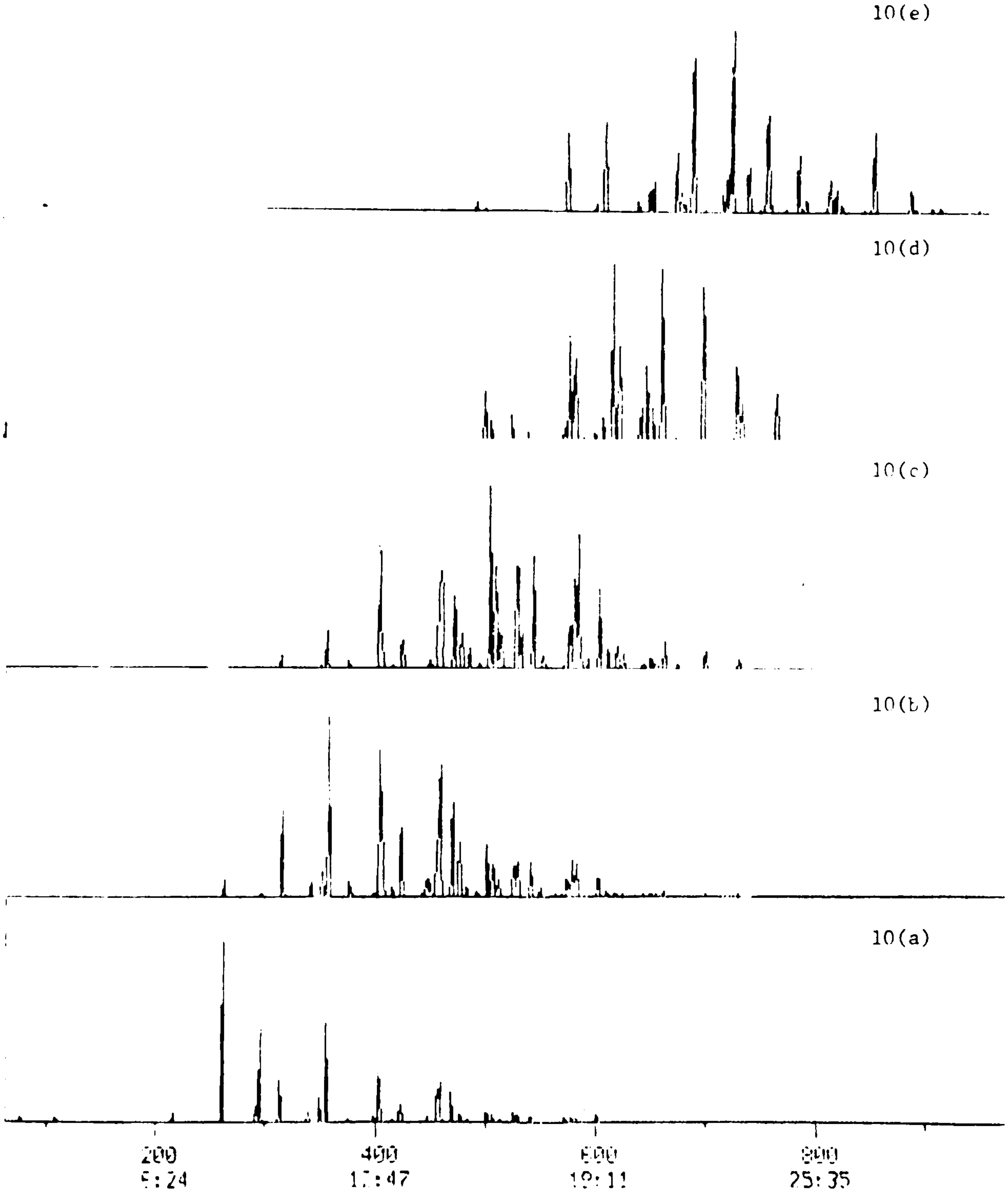
Figure 7 - One of the MID descriptors (A12) that constitutes the scan sequence A1. The particular MID descriptor controlling the quadrupole is changed as the run progresses so that the ions tuned through quadrupole rods are those characteristic of the PCBs eluting from the capillary column at a given time. The time windows when the various MID descriptors are active is shown in Table 5 and were determined from the RICs for the Aroclors run in the full scan mode.



Figures 8(a)-8(e): The RIC's for Aroclors 1232, 1242, 1248, 1254 and 1260 respectively acquired using a full scan from 50 to 500 amus in two seconds.



<u>Figures 9(a)-9(e)</u>: The RIC's for Aroclors 1232, 1242, 1248, 1254 and 1260 respectively acquired using the MID descriptor Q1.



Figures 10(a)-10(e): The RIC's for Aroclors 1232, 1242, 1248, 1254 and 1260 respectively acquired using the MID descriptor sequence AI.

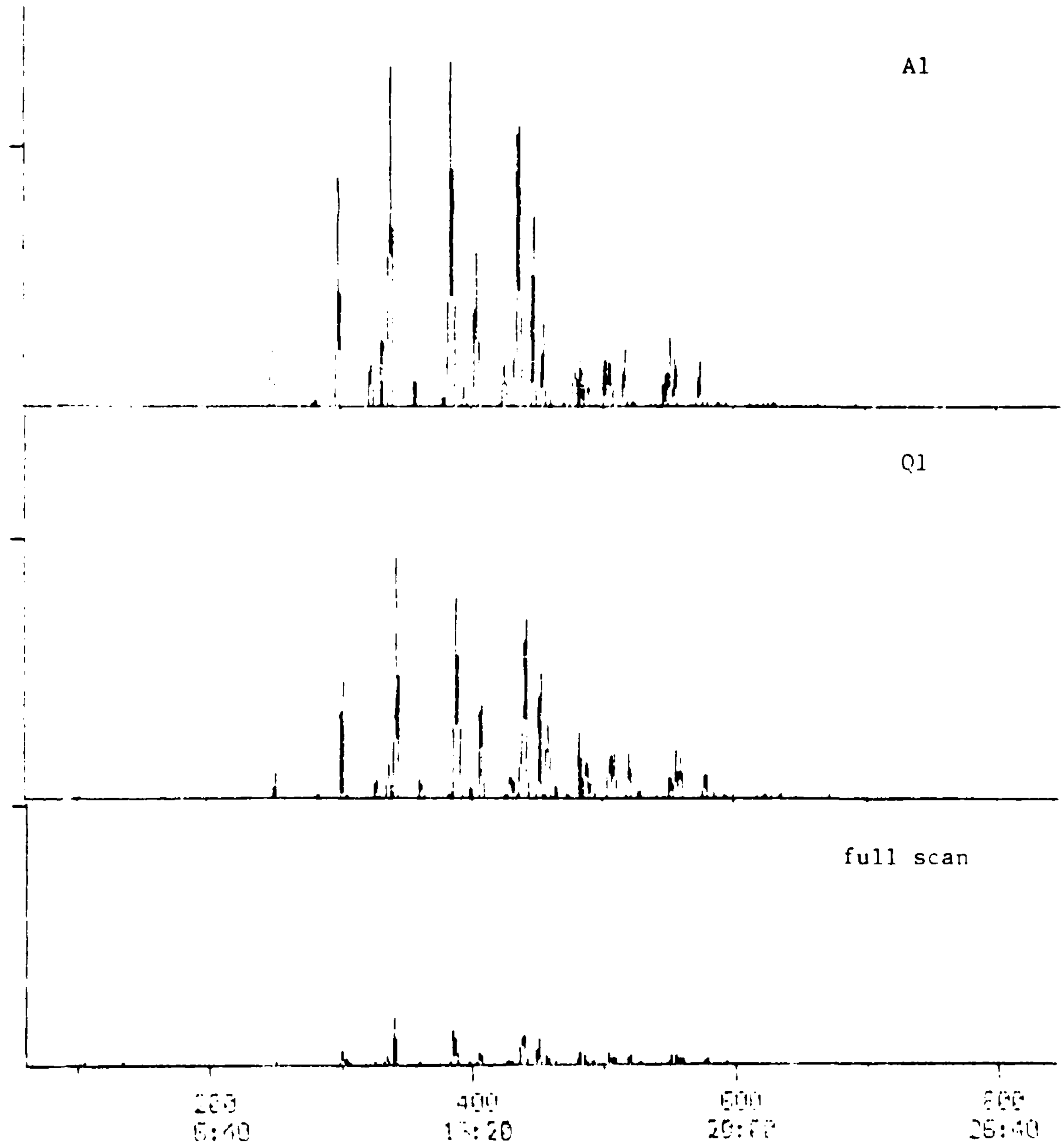


Figure 11(a): Comparison of the RIC's for Aroclors 1242 and 1260 acquired using a full scan, MID descriptor Q1, and MID descriptor sequence A1.

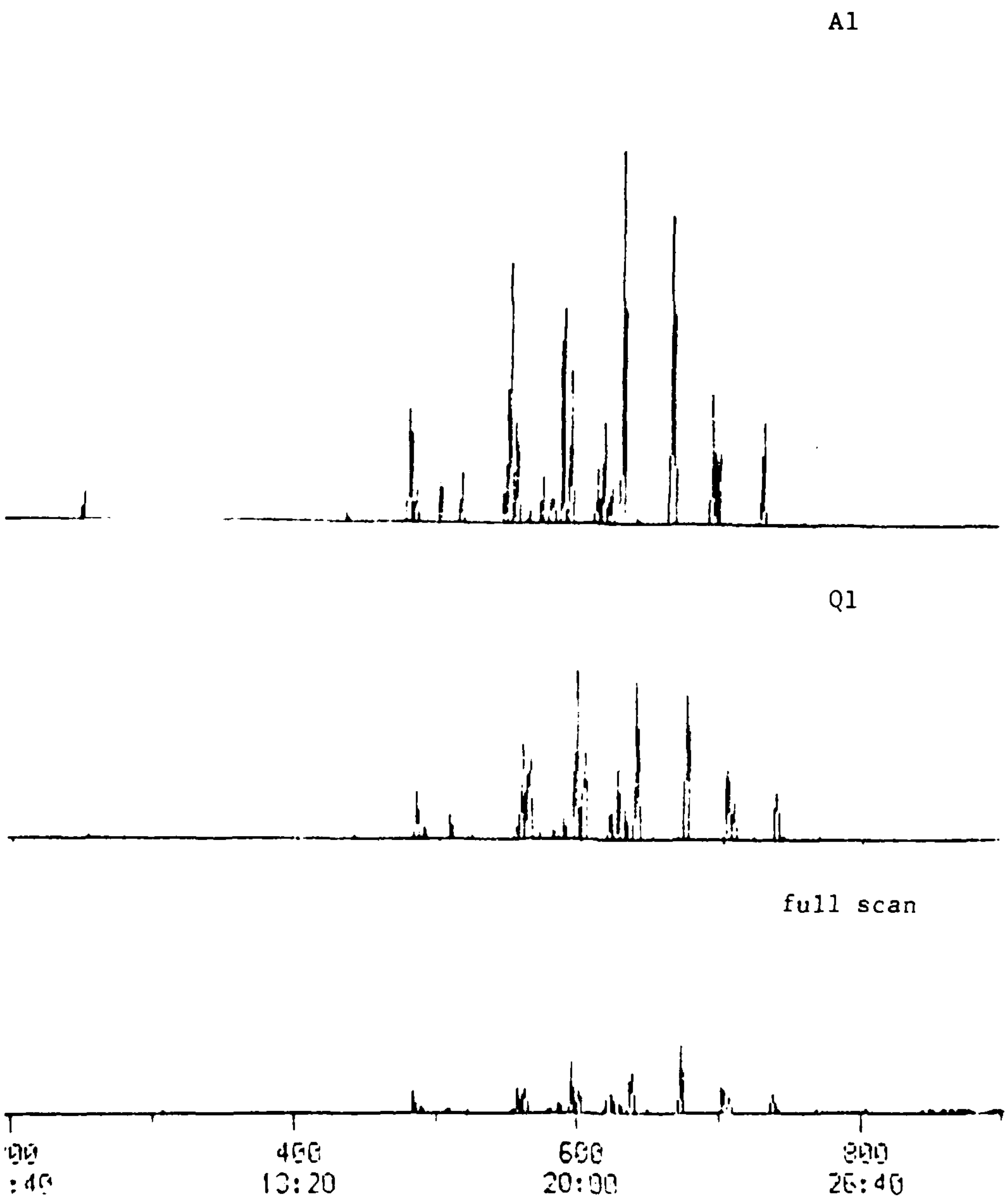
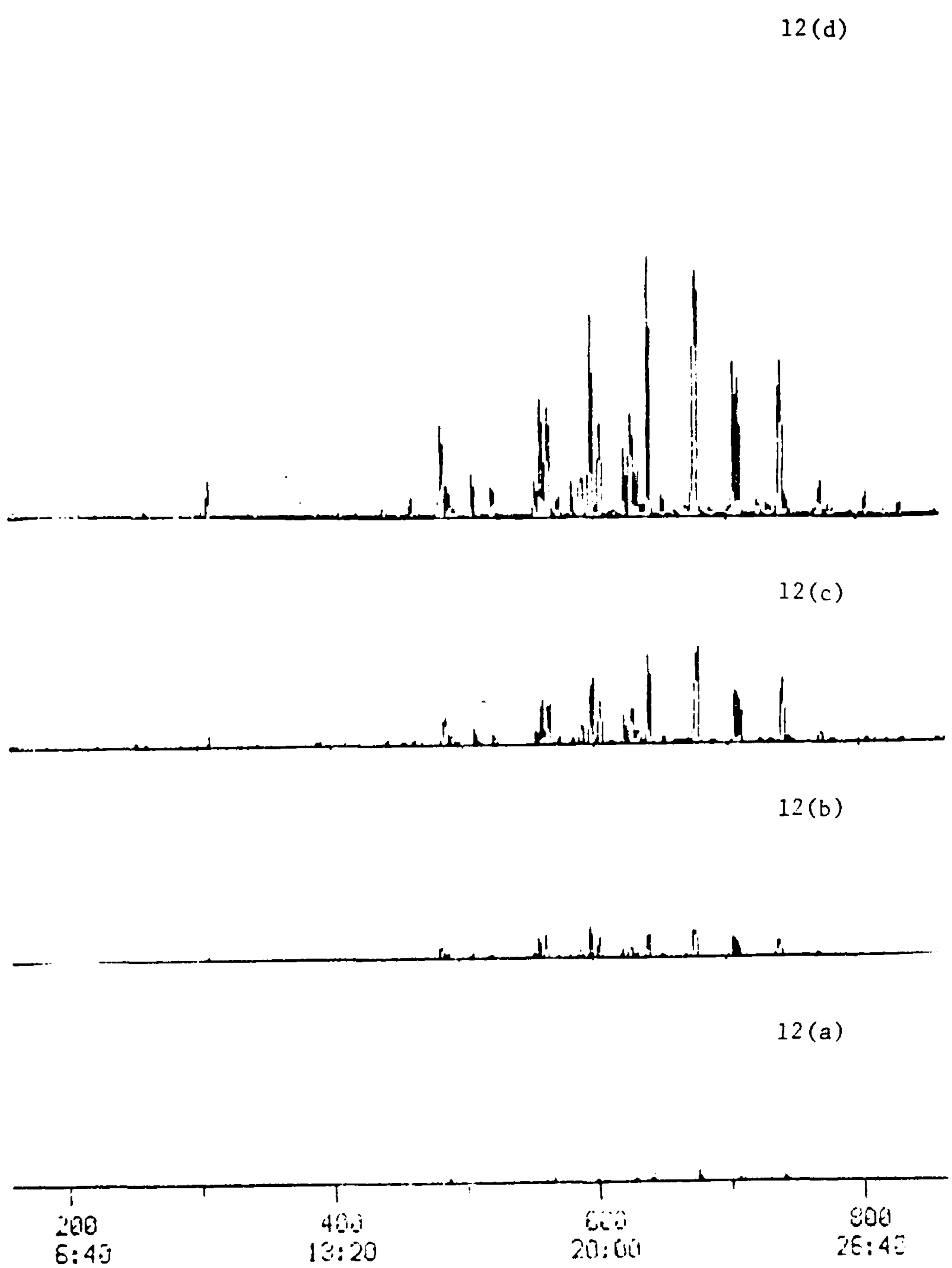


Figure 11(b): Comparison of the RIC's for Aroclors 1242 and 1260 acquired using a full scan, MID descriptor Q1, and MID descriptor sequence A1.



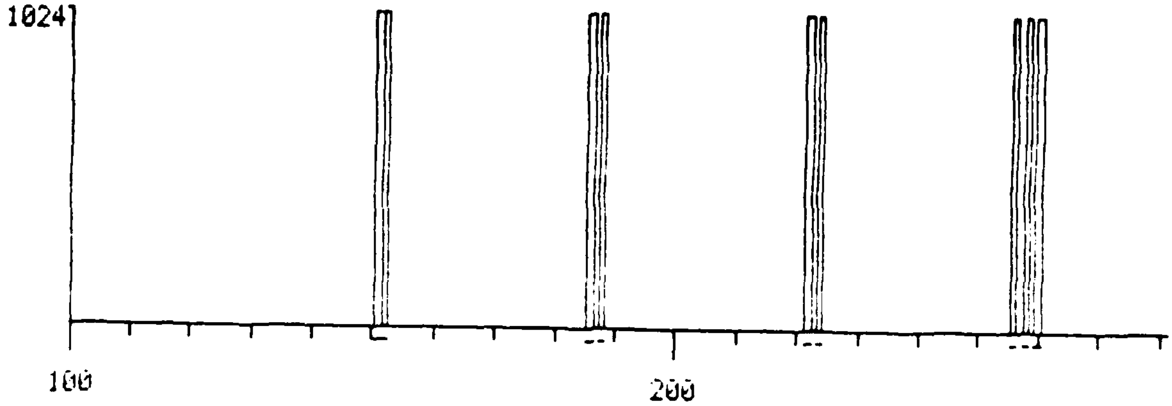
Figures 12(a)-12(d): RIC's of Aroclor 1254 acquired in the full scan mode as the voltage applied to the electron multiplier is increased. The response increases as the voltage is increased from 1300 volts in (a) to 1900 volts in (d) in 200 volt increments.

APPENDIX A

THE MID DESCRIPTORS THAT, TOGETHER WITH MID DESCRIPTOR

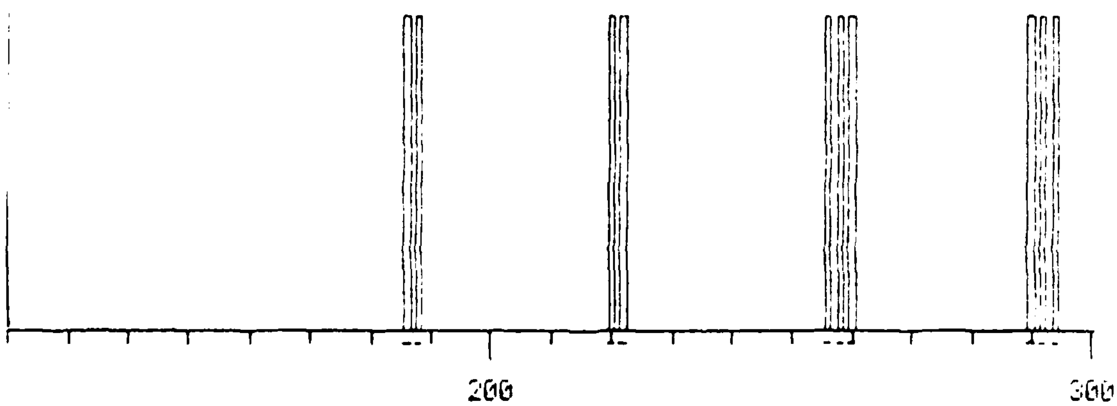
A12, CONSTITUTE THE MID DESCRIPTOR SEQUENCE AI

A23



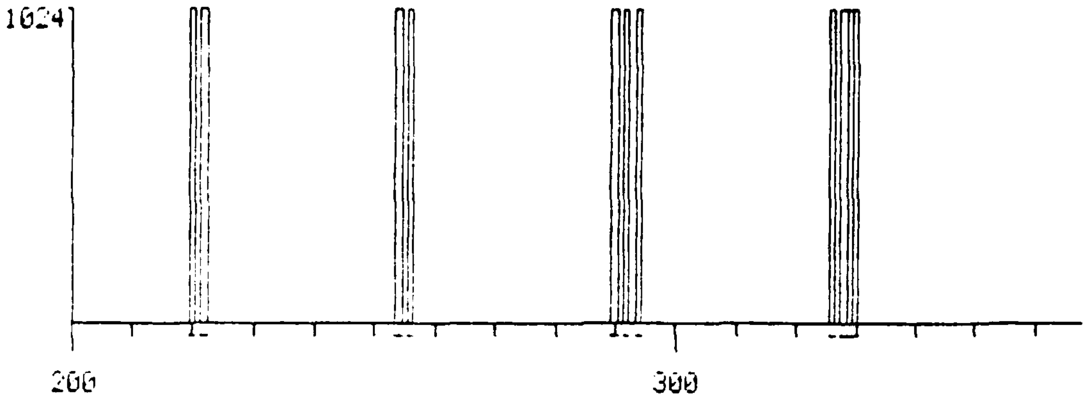
INT #	BEGIN MASS	END MASS	TIME REQUEST
1.	150.394	151.394	0.150
2.	151.394	152.394	0.150
3.	185.370	186.370	0.150
4.	187.368	188.368	0.150
5.	221.345	222.345	0.150
6.	223.343	224.343	0.150
7.	255.321	256.321	0.150
8.	257.319	258.319	0.150
9.	259.318	260.318	0.150

A34



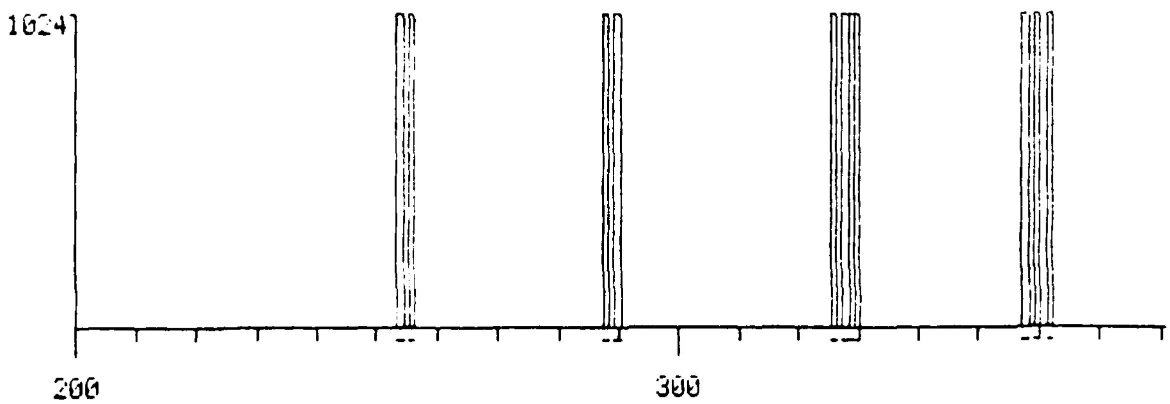
INT #	BEGIN MASS	END MASS	TIME REQUEST
1.	185.370	186.370	0.150
2.	187.368	188.368	0.150
3.	219.346	220.346	0.150
4.	221.345	222.345	0.150
5.	255.321	256.321	0.150
6.	257.319	258.319	0.150
7.	259.318	260.318	0.150
8.	289.297	290.297	0.150
9.	291.295	292.295	0.150
10.	293.294	294.294	0.150

A45



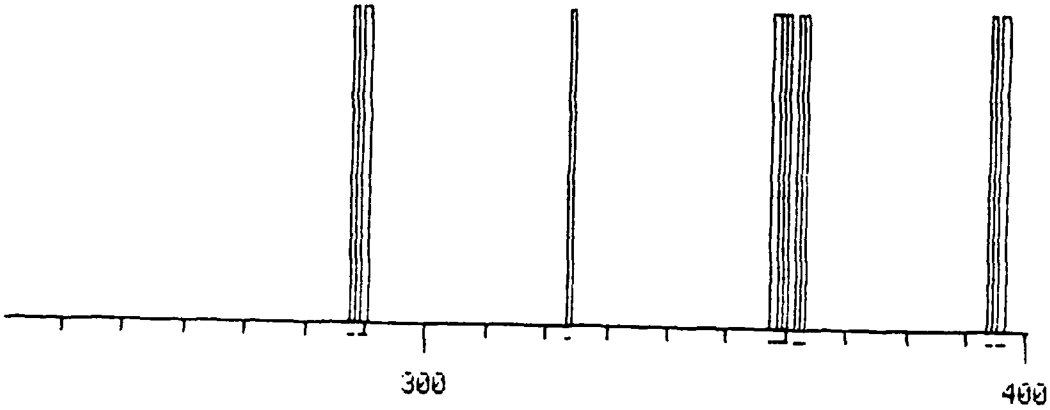
INT #	BEGIN MASS	END MASS	TIME REQUEST
1.	219.346	220.346	0.150
2.	221.345	222.345	0.150
3.	253.322	254.322	0.150
4.	255.321	256.321	0.150
5.	289.297	290.297	0.150
6.	291.295	292.295	0.150
7.	293.294	294.294	0.150
8.	325.271	326.272	0.150
9.	327.270	328.270	0.150
10.	328.270	329.270	0.150
11.	329.270	330.269	0.150

A56



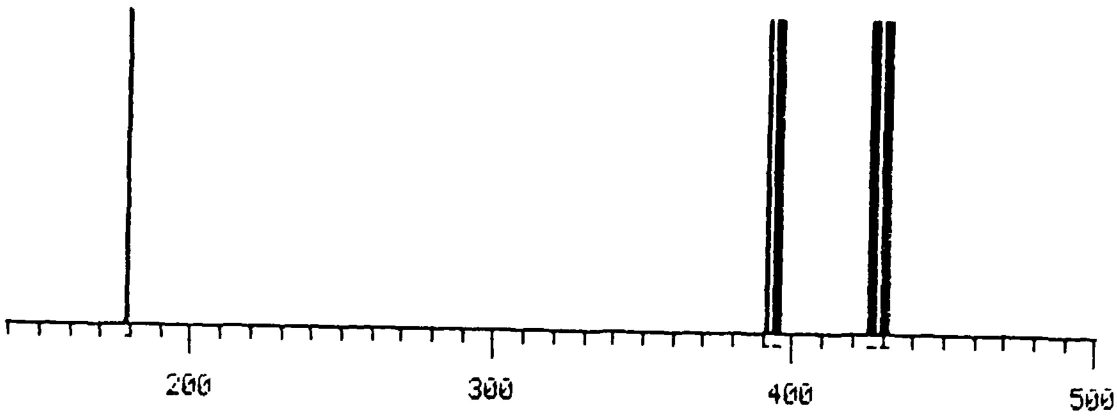
INT #	BEGIN MASS	END MASS	TIME REQUEST
1.	253.322	254.322	0.150
2.	255.321	256.321	0.150
3.	287.298	288.298	0.150
4.	289.297	290.297	0.150
5.	325.271	326.272	0.150
6.	327.270	328.270	0.150
7.	328.270	329.270	0.150
8.	329.270	330.269	0.150
9.	357.249	358.249	0.150
10.	359.248	360.248	0.150
11.	361.246	362.247	0.150

A67



INT #	BEGIN MASS	END MASS	TIME REQUEST
1.	287.298	288.298	0.150
2.	289.297	290.297	0.150
3.	323.273	324.273	0.150
4.	357.249	358.249	0.150
5.	358.249	359.248	0.150
6.	359.248	360.248	0.150
7.	361.246	362.247	0.150
8.	362.247	363.246	0.150
9.	393.224	394.224	0.150
10.	395.222	396.223	0.150

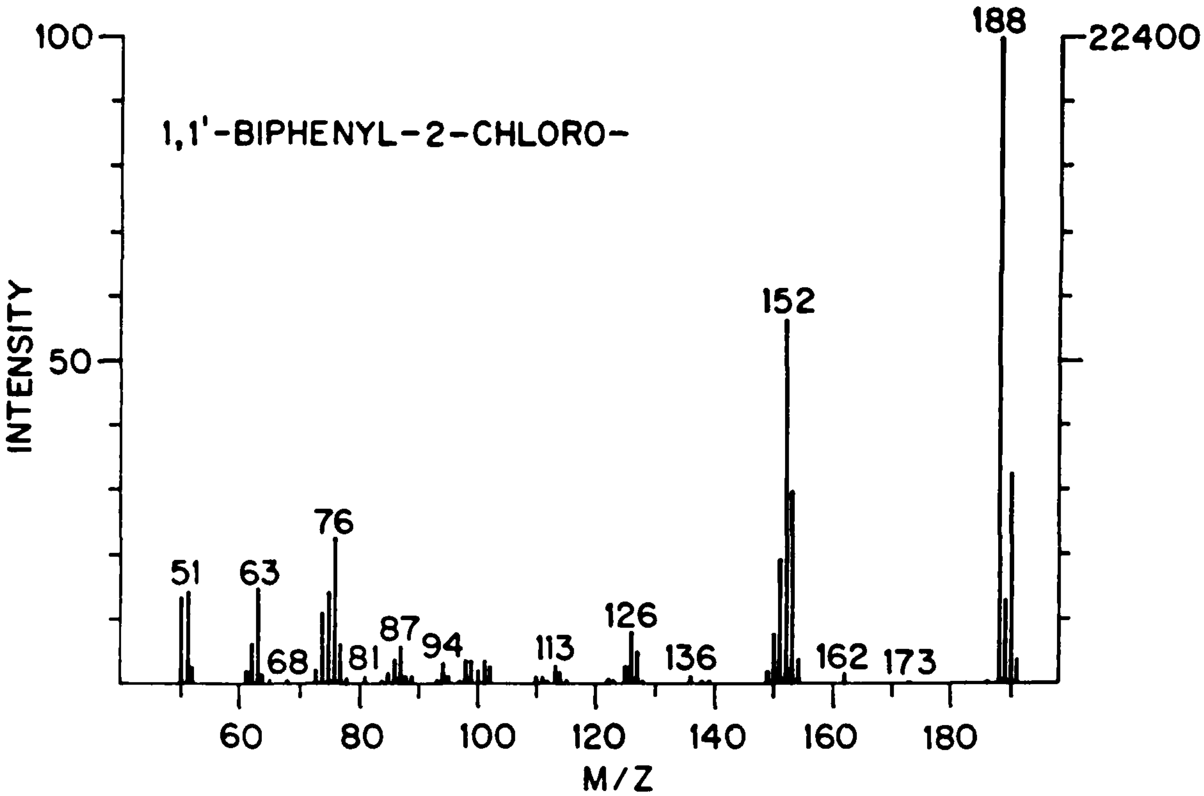
A87



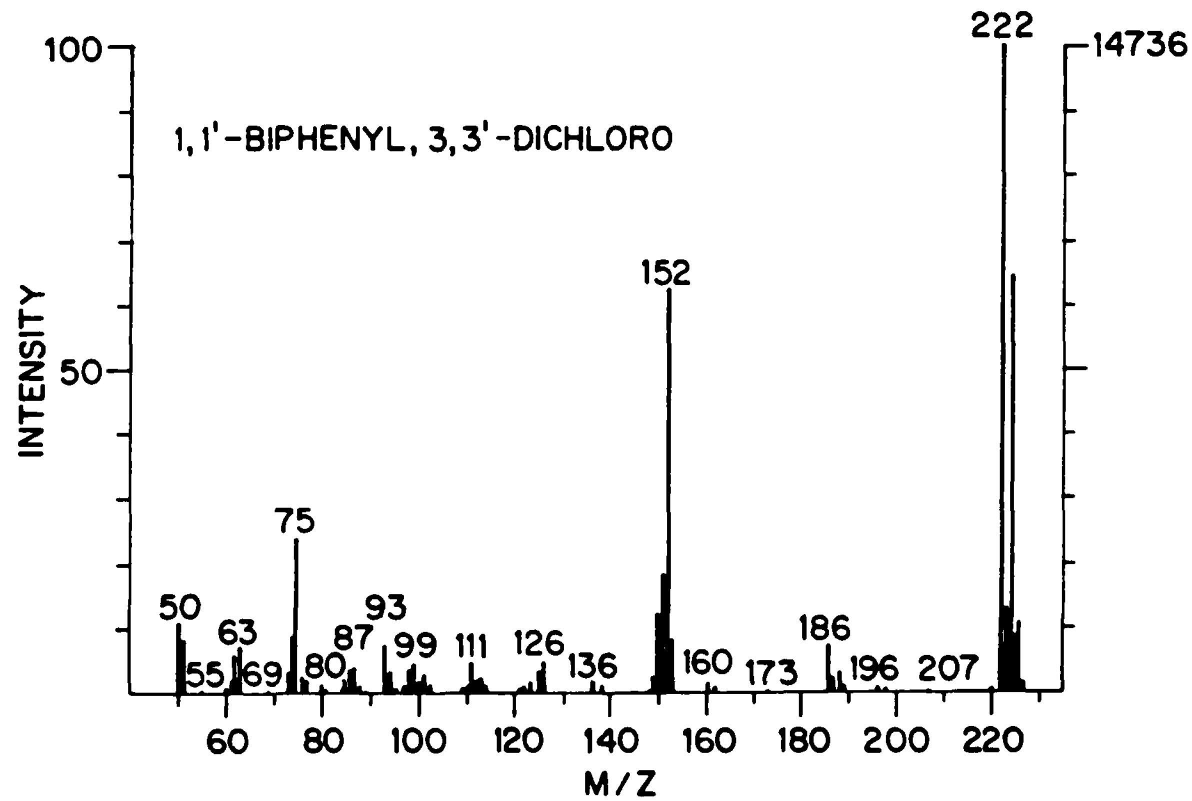
INT #	BEGIN MASS	END MASS	TIME REQUEST
1.	178.375	179.375	0.150
2.	391.225	392.226	0.150
3.	393.224	394.224	0.150
4.	395.222	396.223	0.150
5.	425.201	426.202	0.150
6.	427.200	428.200	0.150
7.	429.199	430.199	0.150
8.	431.197	432.197	0.150

APPENDIX B

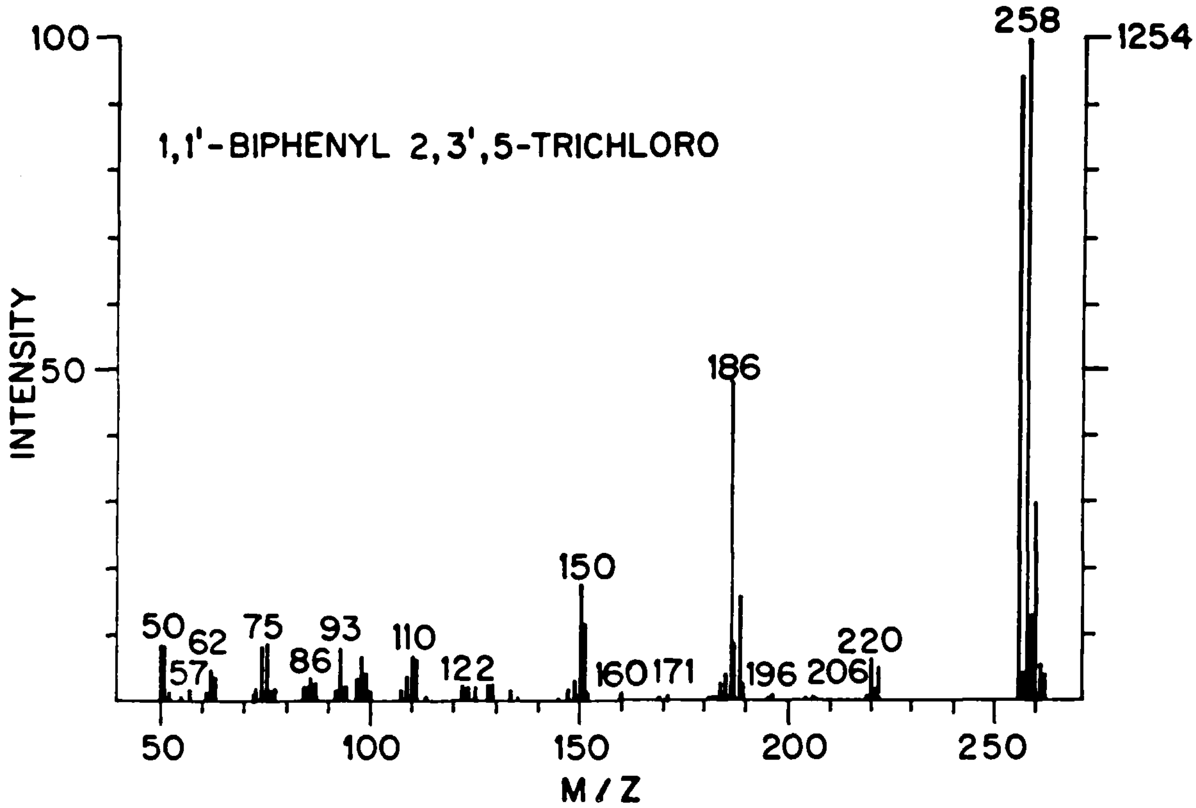
MASS SPECTRA OF SELECTED PCB's



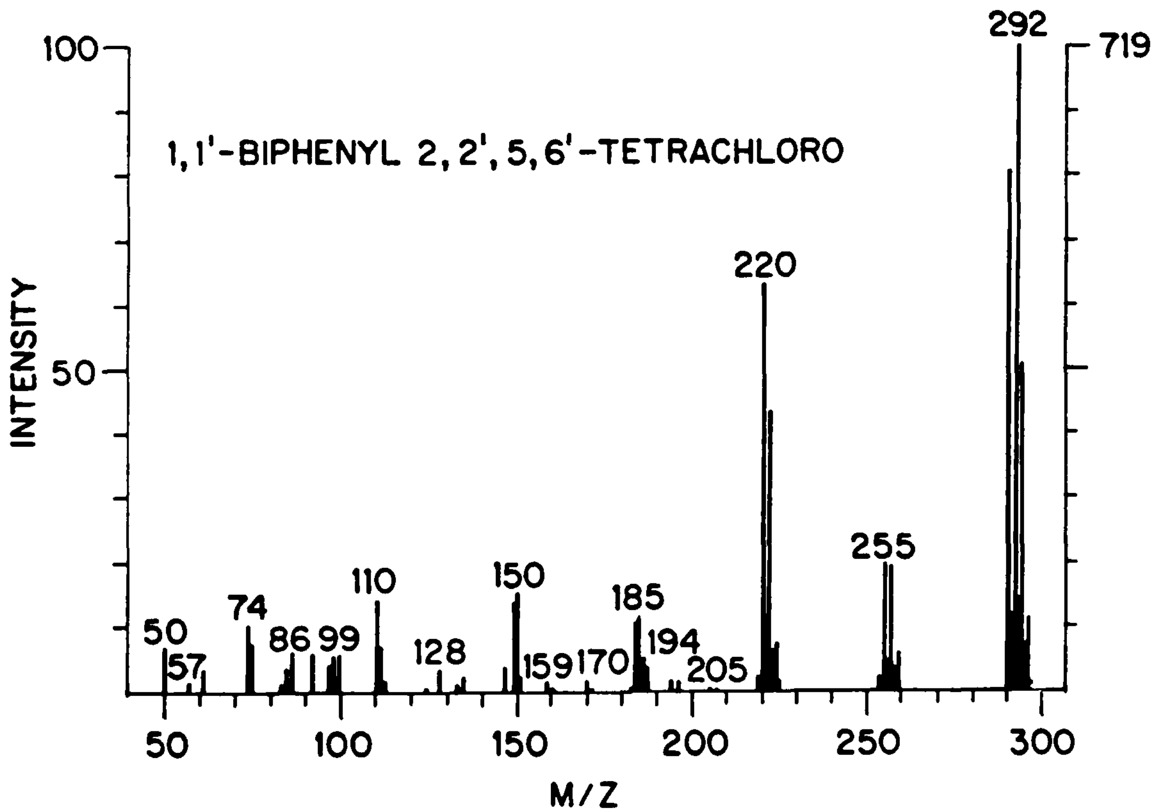
1,1'-BIPHENYL-2-CHLORO-
INTENSITY
M/Z
22400
188
152
76
51
63
68
81
87
94
113
126
136
162
173



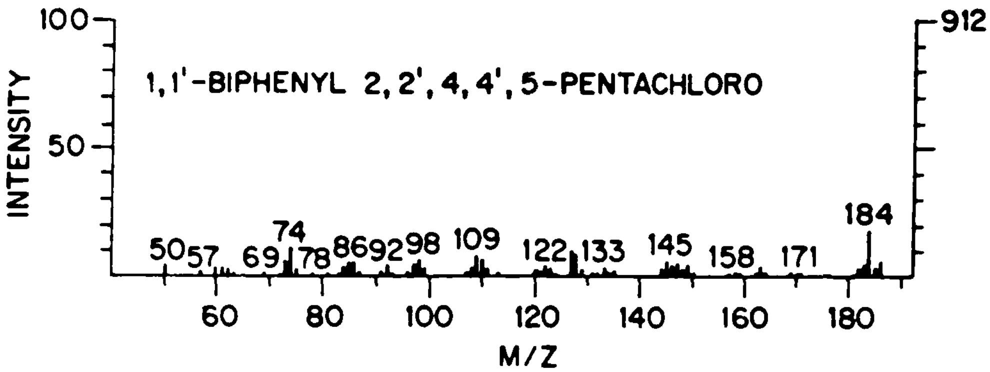
1,1'-BIPHENYL, 3,3'-DICHLORO
INTENSITY
M/Z
14736
222
152
75
50
55
63
69
80
87
93
99
111
126
136
160
173
186
196
207

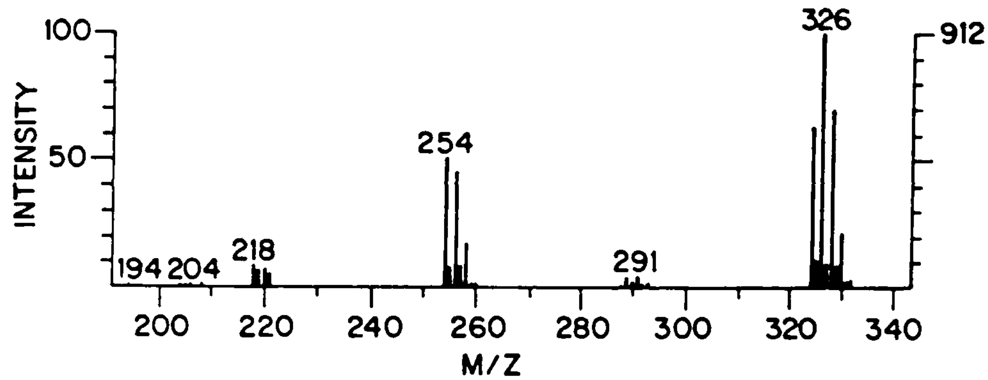


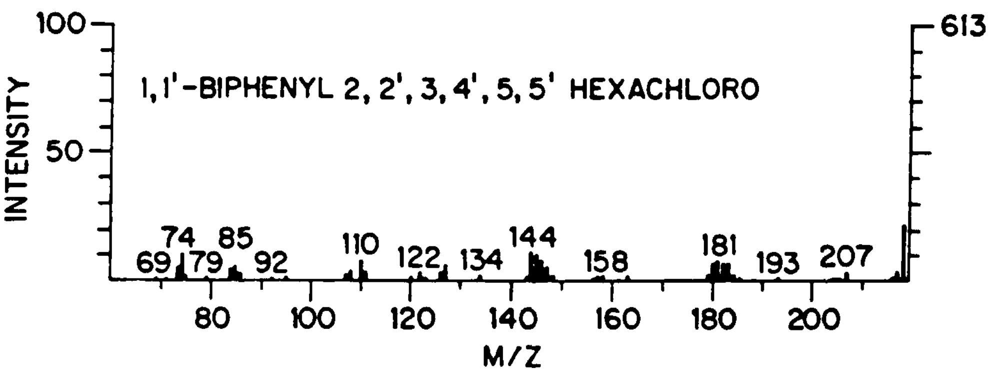
100
50
INTENSITY
1,1'-BIPHENYL 2,3',5-TRICHLORO
258
1254
186
150
50
62
57
75
86
93
110
122
160
171
196
206
220
50
100
150
200
250
M / Z

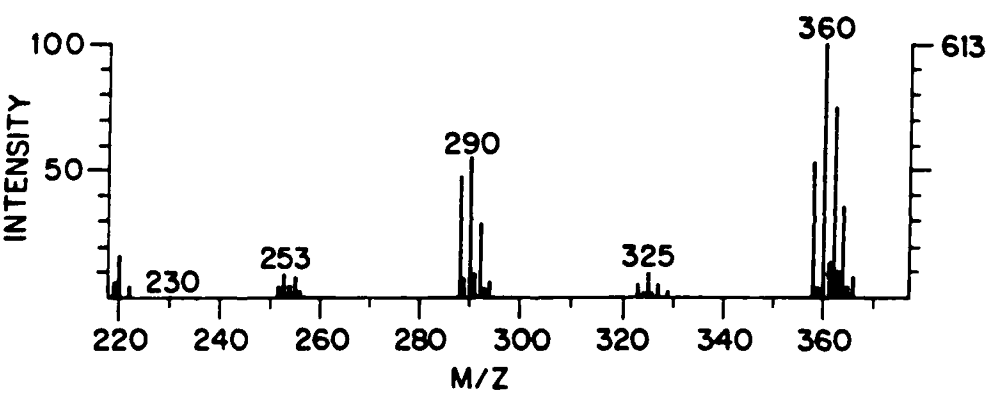


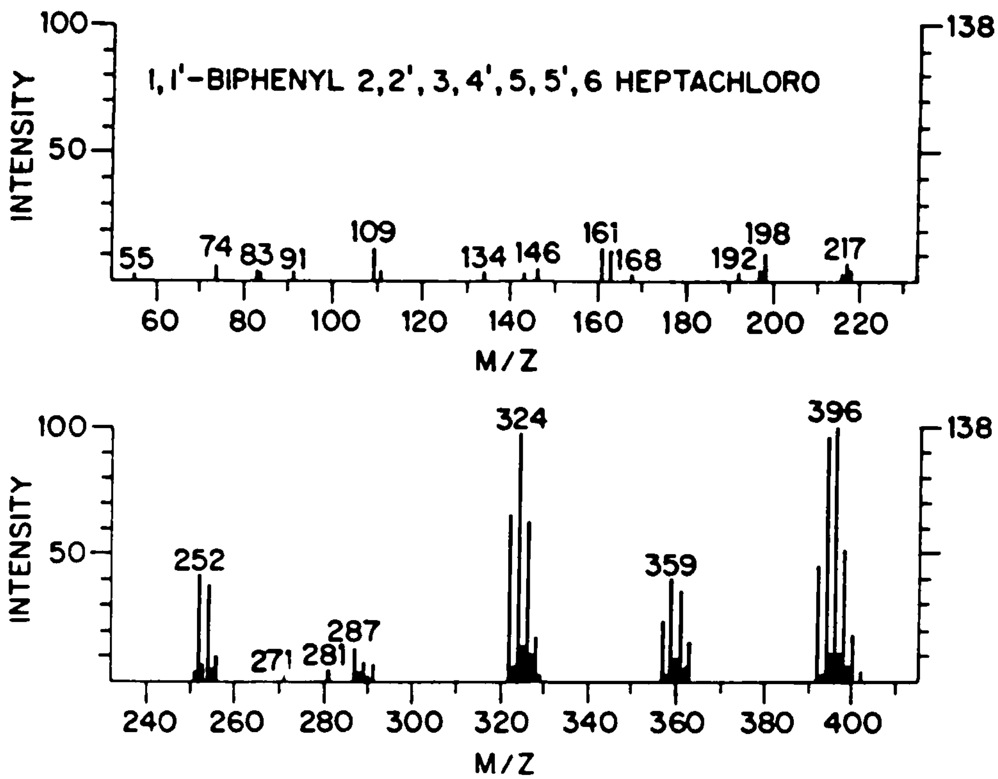
100
50
INTENSITY
1,1'-BIPHENYL 2,2',5,6'-TETRACHLORO
292
719
220
255
150
110
185
74
50
57
86
99
128
159
170
194
205
50
100
150
200
250
300
M/Z

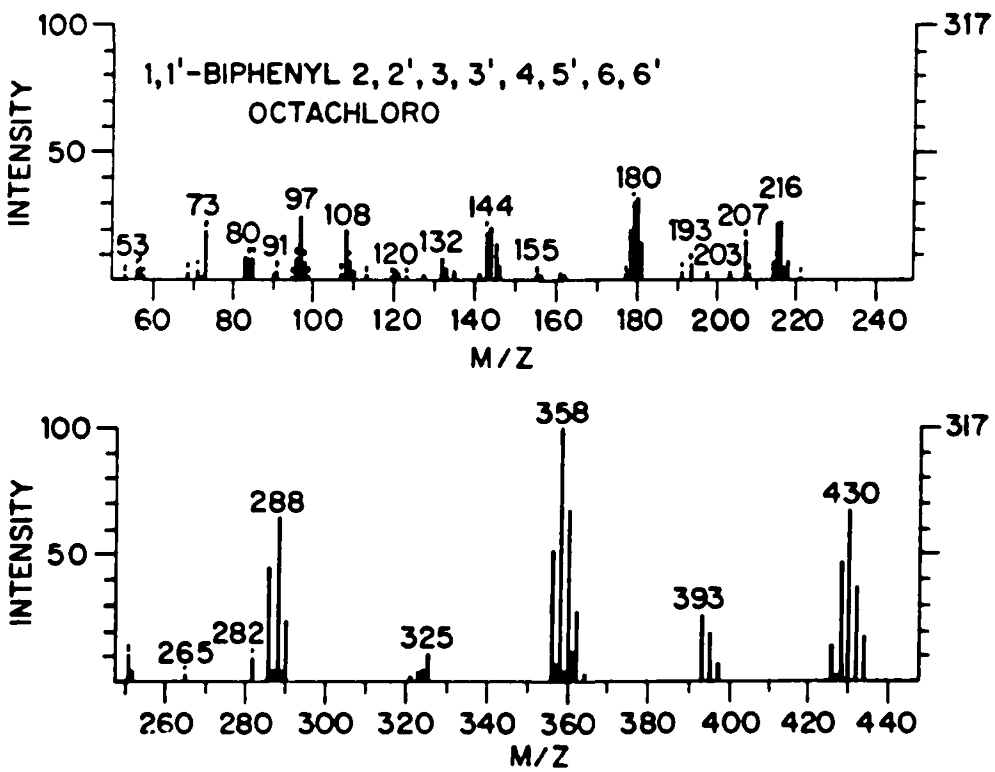

1,1'-BIPHENYL 2,2',4,4',5-PENTACHLORO
INTENSITY
M/Z
100
50
912
50 57 69 74 78 86 92 98 109 122 133 145 158 171 184
60 80 100 120 140 160 180

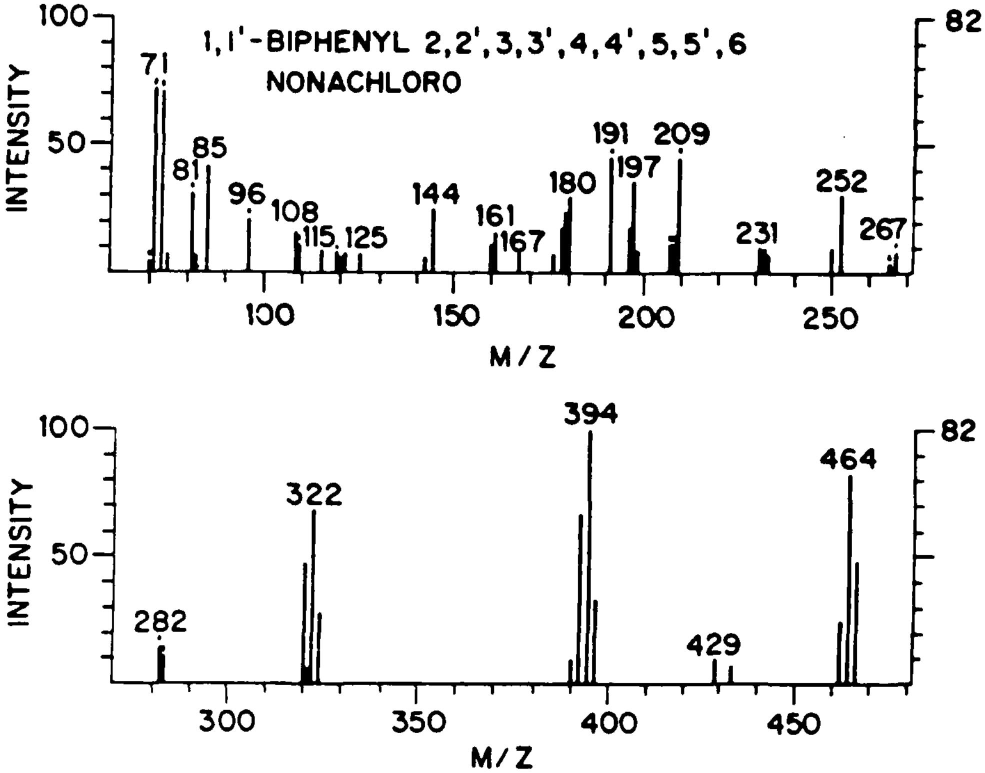
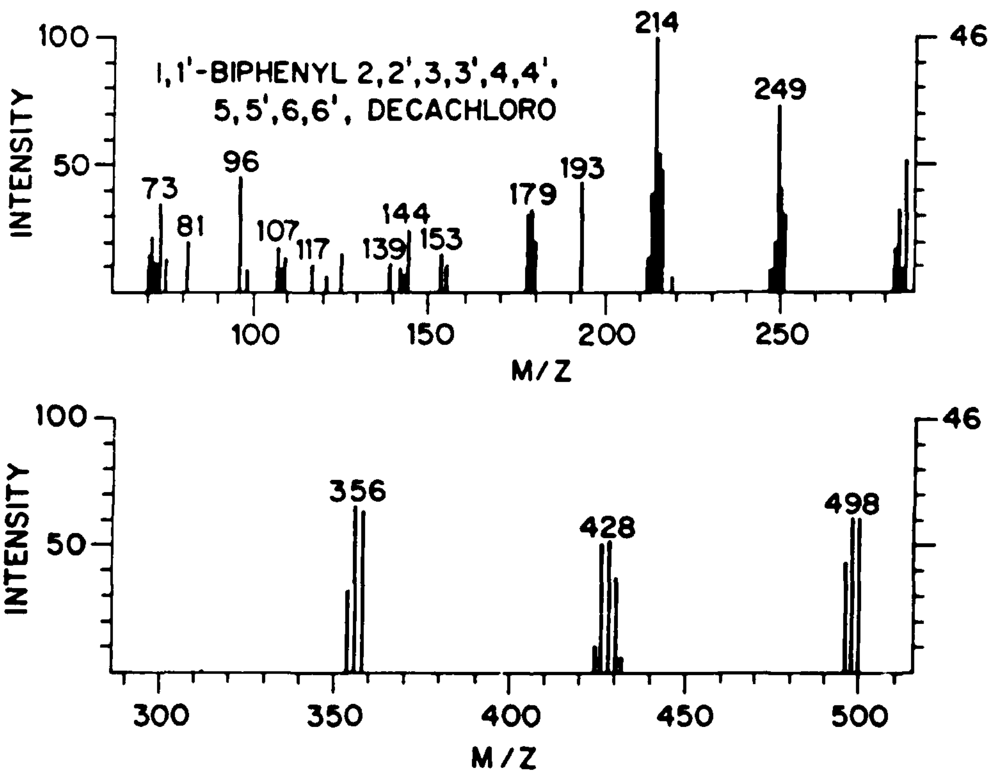

INTENSITY
M/Z
100
50
912
194 204 218 254 291 326
200 220 240 260 280 300 320 340


1,1'-BIPHENYL 2,2',3,4',5,5' HEXACHLORO
INTENSITY
M/Z
100
50
613
69 74 79 85 92 110 122 134 144 158 181 193 207
80 100 120 140 160 180 200


INTENSITY
M/Z
100
50
613
230 253 290 325 360
220 240 260 280 300 320 340 360


1,1'-BIPHENYL 2,2',3,4',5,5',6 HEPTACHLORO
INTENSITY
100
50
138
55
74
83
91
109
134
146
161
168
192
198
217
60 80 100 120 140 160 180 200 220
M/Z
252
271
281
287
324
359
396
240 260 280 300 320 340 360 380 400
M/Z


1,1'-BIPHENYL 2,2',3,3',4,5',6,6'
OCTACHLORO
INTENSITY
100
50
317
53
73
80
91
97
108
120
132
144
155
180
193
203
207
216
60 80 100 120 140 160 180 200 220 240
M/Z
265
282
288
325
358
393
430
260 280 300 320 340 360 380 400 420 440
M/Z


1,1'-BIPHENYL 2,2',3,3',4,4',5,5',6
NONACHLORO
INTENSITY
M/Z
100
50
82
71
81
85
96
108
115
125
144
161
167
180
191
197
209
231
252
267
100
150
200
250
394
322
464
282
429
300
350
400
450

1,1'-BIPHENYL 2,2',3,3',4,4',
5,5',6,6', DECACHLORO
INTENSITY
M/Z
100
50
46
73
81
96
107
117
139
144
153
179
193
214
249
100
150
200
250
356
428
498
300
350
400
450
500

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Unclassified

Security Classification

DOCUMENT CONTROL DATA – R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1 ORIGINATING ACTIVITY Defence Research Establishment Atlantic	2a. DOCUMENT SECURITY CLASSIFICATION Unclassified 2b GROUP

3 DOCUMENT TITLE

Optimization of the Finnigan MAT 5100 Capillary Gas Chromatograph-Mass Spectrometer for the Analysis of Polychlorinated Biphenyls

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

5 AUTHOR(S) (Last name, first name, middle initial)

J.A. Hiltz and J.J. Power

6 DOCUMENT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
November 1986	48	12

8a. PROJECT OR GRANT NO.	9a ORIGINATOR'S DOCUMENT NUMBER(S) DREA Technical Memorandum 86/222
8b CONTRACT NO.	9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)

10 DISTRIBUTION STATEMENT

Unlimited Distribution

11 SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY Defence Research Establishment (A)

13 ABSTRACT

The basis of operation of a capillary gas chromatograph with a quadrupole mass spectrometer as a detector is reviewed. This is followed by the description of the optimization of a Finnigan MAT 5100 gas chromatograph-mass spectrometer-data system (GC/MS/DS) for the detection and identification of PCBs. In particular, the effects of increasing electron multiplier voltage and the use of multiple ion detection (MID) scan sequences on the sensitivity of the quadrupole mass spectrometer are investigated. Both increasing the electron multiplier voltage and the use of specialized MID scan sequences were found to result in an improved detector response.

DSIS 78-070

KEY WORDS

polychlorinated biphenyls
PCBs
detection
capillary gas chromatograph
quadrupole mass spectrometer
sensitivity

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